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PHYSICAL PROPERTIES OF FOODS-2

Edited by

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PHYSICAL PROPERTIES OF FOODS—2

Proceedings of a Seminar held under the auspices of COST (European Cooperation in Scientific and Technical Research) to mark the conclusion of the COST 90bis Project on the physical properties of foods. The Seminar was organised by the Executive Committee of COST 90bis in collaboration with the Commission of the European Communities, the Department of Food Science, Swiss Federal Institute of Technology, Zürich, Switzerland, and the Green Meadow Foundation, Gottlieb Duttweiler Institute, Zürich, Switzerland.

PHYSICAL PROPERTIES OF FOODS—2

COST 90bis Final Seminar Proceedings

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Foreword

Although the term 'food' in relation to science, technology and engineering might not conjure up an immediate picture of 'hi-tech' activity at the frontiers of knowledge in comparison with such widely-publicised subjects as genetic engineering, microelectronics or robotics, it is nevertheless a fact that food science, technology and engineering must maintain the same up-to-date interface with basic scientific progress as more 'glamorous' activities. Indeed, improvements in the availability and quality of foodstuffs by genetic manipulation, the control and optimisation of food processes by microelectronics and the use of robotics in food operations and quality control represent both important applications and special challenges for such modern developments as the three examples quoted. The successful application of the latest scientific and engineering developments to the real world of food can surely have no equal in terms of value, interest and worthwhileness to mankind and in its importance to developed and developing societies alike.

The complexity of food systems demands an integrated, interdisciplinary approach and their scale and importance makes it all the more desirable for isolated research to be superseded by coordinated international research. This is equally true in relation to the highly competitive, sophisticated and varied food systems of industrialised nations which are now largely in conditions of surplus in relation to the more urgent and basic needs of developing countries for greater quantity and quality of food at the points of consumption. In both cases there is the requirement to provide the consumer with wholesome, nutritious and enjoyable food, convenient in use, available when required and reasonable in price.

COST (European Cooperation in Scientific and Technological Research)

has long recognised the importance of food research in the industrial, economic and social development of its nineteen constituent European States and since the emergence during 1974–78 of suitable structures and priorities for cooperation and coordination, COST has played an active role in promoting international action in important selected areas of food research. This has led to the establishment of a network of institutions and individuals throughout Europe committed to and experienced in the 'European dimension' of scientific and technical development directed towards benefiting both food industry and consumer.

The COST 90bis Project on The Physical Properties of Foods which is the subject of this volume is embedded both in the general food research situation and in the attempt to coordinate such research at the European level. The text not only reports on the scientific outcome of the Project, it also reviews critically the cooperative procedures used in the belief, on the part of the organisers of the Seminar at which these papers were presented, that the unique experience of COST should be displayed in terms which go well beyond the simple recording of technical information on physical properties of foods. For this reason the reader will find, along with technical information, some general reflections on food research by COST Member States and the Commission of the European Communities. Additional publications will contain further scientific and technological results arising from this Project.

The COST 90bis Final Seminar was held in Rüschlikon/Zürich exactly 5 years after the Final Seminar of COST 90 in Leuven. Considering the fact that cooperation on a European level between a large number of institutions on several facets of a complex subject at the same time cannot be expected to be less trouble-free than the corresponding work in any one institution or country, progress by the Project in the second 4-year period may be regarded as again substantial. The availability of reliable information on physical properties of foods, whether it be specific quantitative data or guidance on reliable means of measurement, must be an obvious and logical prerequisite to progress in almost any sector of food science, food technology and food engineering. Even so, more than 18 years have passed since the COST 90bis Project Leader, Ronald Jowitt, together with Charles Jason of the Torry Research Station, addressed the Third European Food Symposium of the European Federation of Chemical Engineering Food Working Party in Bristol and stressed 'the need for a detailed knowledge of basic physical properties of foodstuffs in relation to process and plant design'.

It is appropriate to quote the German saying 'Gut Ding will Weile'

haben'* and gratefully acknowledge that the COST 90bis Project Leader did not cease to pursue this important goal in food research over all these years. Thanks are due to him for his contributions to the COST 90bis Project, especially for his accomplishments as Senior Editor of these Proceedings. Thanks are also due to the Commission of the European Communities and to the participating Community and Non-Community COST Member States for allocating administrative or technical resources in various ways. Finally, special thanks are extended to all individuals from public and private research and educational institutions and from industry who contributed their expertise towards the common goal of Project COST 90bis, Physical Properties of Foods—2.

FELIX ESCHER

* Freely translated: 'Anything worthwhile takes time', or, 'Nothing good is achieved in a hurry'. Ed.

Preface

This volume is both a contribution to the subject of physical properties of foods and an account rendered. In these respects it is a sequel to the proceedings of the Final Seminar of COST 90, *Physical Properties of Foods* (edited by R. Jowitt *et al.*, Elsevier Applied Science Publishers, London, 1983) and is arranged in a similar way.

The first chapter is an overview of Project COST 90bis—its origins, objectives, organisation, personalities and achievements. Chapters 2–12 are concerned with diffusion in foods and as in the case of the other subjects include a contribution from outside COST on a significant aspect of the subject. Chapters 13–20 report on current and collaborative work on electrical properties of foods and their industrial significance. In Chapters 21–28 optical properties of foods are considered, in particular, collaborative ‘calibration’ experiments and the practical and industrial significance of the colour of foods. Chapters 29–38 deal with the principles of and the COST collaborative work on mechanical properties of foods including food powders. Chapters 39–42 deal with the subject of data collection, handling and dissemination, both within and outside COST 90bis, and on food and non-food materials. The closing chapters consider, in turn, some conclusions to be drawn from the Project’s work, what should follow it and its relationship to wider issues.

The subject areas are, of course, different from those of the preceding volume and a further difference is the inclusion of adaptations of posters displayed at the Seminar. These follow the main chapters on the respective subjects. As before, a transcript by the Project Leader of the discussion which followed the presentation of the papers at the Seminar is included and follows the corresponding chapters which the papers now form.

Following the papers on Diffusion at the Seminar, an interesting, brief,

unscheduled presentation with figures was made by E. U. Schlünder of Karlsruhe on diffusion of binary mixtures of volatiles through porous media on drying. This and the ensuing discussion was recorded and both were intended to be included in these proceedings. We regret that efforts to obtain the MS and the figures used in time were not successful and so a summary has been produced by the Editor (RJ) based on the recording of the presentation and other publications by the author, at his suggestion.

Responsibility for editing these Proceedings has fallen in the first place on the Chairmen of the corresponding Project committees with overall editorial responsibility resting on the Project Leader:

Chairman

COST-Community Coordinating Committee and Executive Committee	F. Escher, ETH, Zürich
Diffusion Properties Subgroup	M. Roques, ENSIC, Nancy
Electrical/Optical Properties Subgroup	M. Kent, Torry Research Station, Aberdeen
Mechanical Properties Subgroup	B. McKenna, University College, Dublin
Data Subgroup	R. Jowitt, COST 90bis Project Leader

The extent—if any—to which authors' and participants' affiliations should be anglicised in such a publication has been given careful thought. Some participants automatically anglicise their institutions' names and descriptions for use outside their homelands whereas others—quite understandably—would not think of doing so. In between there are those who sometimes do and sometimes do not. A policy of even-handedness has been adopted here such that when affiliations are being cited for information or description (as in lists of collaborators, for example) they are all anglicised without exception and when they denote an address for communication or probable communication they are uniformly presented in the 'home' language. Two minor deviations from this rule are that where institutions are well-known by their acronym—'SIK' or 'ENSBANA' for example—these are retained along with the anglicised names, and where participants themselves usually give their names and addresses in English for communication, this is used in *both* cases. We believe this offers the best of all three worlds—maximum information, speediest communication and, not least, consistency.

Acknowledgement must also be made of the valuable assistance of M. Rüegg (Federal Dairy Research Station, Liebefeld-Bern) in collecting

and collating the poster transcripts; of P. Tobback's (Catholic University of Leuven) initial Chairmanship of the Diffusion Properties Subgroup from 1983 to 1984; of F. Escher and colleagues W. Denzler, R. Genner-Ritzmann, M. Rüegg and M. Stein's organisation of the Final Seminar in Rüschlikon, Zürich and the Green Meadow Foundation/Gottlieb Duttweiler Institute, Rüschlikon/Zürich Federation of MIGROS Co-operatives, Zürich's and the Federal Office for Education and Science, Bern's generous financial support of it; of G. Vos's and C. Sakaloglou's consistent provision of the European Commission's inputs; of I. M. V. Adam's (MAFF, London) valuable help with records of a number of meetings; of the generous facilities, time and hospitality of those (and their organisations) who hosted the many meetings throughout Europe; of all the written contributions including those from invited speakers from outside the Project; and finally of all those dedicated, willing and often enthusiastic contributions from the many participants—especially the Subgroup Chairmen—without which this further exercise in international cooperation on the physical properties of foods would not have been possible.

RONALD JOWITT

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COST 90bis in Perspective

RONALD JOWITT
COST 90bis Project Leader

INTRODUCTION

COST 90 ran from 25 February 1978 until 24 February 1981 and was then extended until 19 March 1982. Its work was fully documented, notably but not exclusively in the Proceedings of its final Seminar in Leuven, Belgium, in September 1981 (Jowitt, R. et al., 1983). It was then succeeded on 15 December 1982 by COST 90bis, a four-year Project scheduled to end on 14 December 1986 (now extended to 31 December 1987). COST 90 was the first COST project in Food Technology. It was set up to coordinate and promote physical property data-producing activity in relation to foods in the Participating States, specifically on the sorption, thermal and liquid rheological properties of foods. The 12 Participating States comprised the then 9 Community States plus Finland, Sweden and Switzerland. It was always known to be impracticable to deal with the whole field of physical properties of foods (ppfs) in the first Project and it was hoped that, given reasonable success with COST 90, plus continuing interest and available funds, a further, similar, cooperative effort on other properties would follow COST 90.

COST 90bis was that sequel, although its first year was devoted to concluding the work of the three subject groups of COST 90. For the last 3 of its original 4 years COST 90bis was concerned with the mechanical, diffusional and electromagnetic (including optical) properties of foods and with data management. Finland did not join COST 90bis but the original nine Members of the Community in COST 90 were joined in COST 90bis by Sweden, Switzerland and by Greece and Spain, both Members of the Community by the end of the Project.

The Chairman of the Mechanical Properties Subgroup throughout was

Brian McKenna of University College, Dublin, and the Subgroup met on six occasions: in Dublin, Leuven, Karlsruhe, Valencia, Lyngby and Naples.

The Electrical/Optical Properties Subgroup was Chaired throughout by Mike Kent of the Torry Research Station, Aberdeen (who also Chaired the Thermal Properties Subgroup during its final year's work within COST 90bis). Although this Subgroup dealt with the distinct subjects of dielectric/microwave interactions of foods and the optical properties—principally the *colour*—of foods, the two 'halves' nevertheless met on the same occasions with broadly common membership. They also met six times: in Dublin, Brussels, Gothenberg, Aberdeen, Cork and Paris.

The Diffusional Properties Subgroup was first Chaired by Paul Tobback of the Catholic University, Leuven, and then (from October 1984) by Michel Roques of the Ecole Nationale Supérieur des Industries Chimiques (ENSIC), Nancy. It met five times: in Dublin, Leuven, Nancy, Liebefeld (Berne) and Valencia.

The Data Subgroup was concerned with the collection and management of ppfs data, mainly that from the other subgroups. It consisted of the chairmen of the other subgroups along with some specialist individual members under the Chairmanship of the Project Leader. It met twice towards the later part of the Project in Brussels and Zürich.

As in the case of COST 90, a Cost-Community Coordinating Committee (CCCC) comprising a Representative from each Participating State and the Commission of the European Communities (CEC) and the Project Leader met annually, normally in Brussels. An extra meeting was held in Lund, Sweden, in September 1985 in order to consider proposals for future activities in ppfs. The informal 'Executive' of COST 90, comprising the Project's office-holders, was formalised and enlarged in COST 90bis.* It met on average twice a year and reviewed the work of the Project as between the different Subgroups and generally. The Chairman of the CCCC and the Executive Committee was Felix Escher of ETH Zürich and the vice-Chairman was Bengt Hallström of Lund University.†

HOW COST 90bis WORKED

The Council of Ministers of the European Community, by its Decision of 22/11/82 (Official Journal L353/25 of 15/12/82), willed COST 90bis into

* It comprised the office-holders plus Walter Spiess of the Federal German Research Institute for Nutrition, Karlsruhe.

† Gilbert Vos, assisted by Caroline Sakaloglou, represented the Commission in the Project and acted as Secretary of the CCCC and Executive Committee.

being, with terms of reference, the structure described above, a budget and key personnel. As in COST 90, Participating States were responsible for the choice, management and funding of their own inputs to the Project. The Commission, along with the Project Leader, were given responsibility for coordination and the Chairmen of the various committees were appointed by the CCCC.

The first meetings of the three subject Subgroups were convened in Dublin at the time of the 6th International Congress of Food Science and Technology and the Third International Congress on Engineering and Food in September 1983 so as to maximise awareness of, and informedness about, COST 90bis. The Subgroup Chairmen and the Project Leader had drawn up various proposals for subjects to be studied and acted upon jointly in the light of information from the Participating States. Experts from those States were invited to these inaugural meetings, one objective of which was for participants to undertake an initial 'calibration' experiment. This would involve determining, in an agreed manner, an appropriate property of a food or food-like material to be provided to all participants from a common source.

The purpose of this initial exercise was to determine how closely the different experimenters' measurements agreed on what was, as far as could be ensured, the same quantity. The first examples chosen were: the response to compression of two kinds of proprietary sweets ('Polo' and 'Silver' mints); the 'diffusivity' of water by the drying of beds of glass microspheres; the dielectric properties of water in the form of carageenan gels with and without added sucrose; and the colour of selected standard colour cards.

The results of these and subsequent coordinated measurements on 'identical' material are described elsewhere in detail. Their usefulness varied but was considerable in all cases. Although the benefits and the problems encountered differed between the different groups, there is no doubt that such a 'calibration' operation is a necessary preliminary to any concerted action of this kind. In most subject groups, at least one set of matching results was obtained from which it was possible to conclude that those laboratories could be relied on to obtain equally valid results when measuring the same property of a particular material.

This was a most important outcome since without such reasonable reassurance the question would always remain as to whether reported differences between values for a particular property of a specified material were 'true' differences, i.e. the property really was different in the different cases, or 'apparent', i.e. the property actually had the same value but the *measured* values of it differed.

Now that these 'calibrated' groups of experimenters have been established for the different properties it would be a great loss if they were not able to be kept 'calibrated' and used actively in the future.

Not surprisingly, not all the results of all the properties measured on all the 'standard' materials agreed within statistically acceptable limits. There were almost always some 'outliers' and the reasons for them often led to useful information of specific or general applicability. Some calibration exercises failed because the 'standard' material proved to be far from standard in the property of interest when tested. A case in point was the mechanical properties of gels made up according to a rigorous method which had previously been found to give reproducible and consistent results in the laboratory recommending it. Clearly, the 'standards' used in such work should be capable of verification by the originator on the actual material as used by calibrants. The mechanical response of this gel was evidently not uniquely determined by the formulation and method of preparation employed on this occasion. The question will immediately spring to mind as to how it was possible to know that these differences were intrinsic to the prepared gels and not due to *apparent* differences between the labs concerned. It is possible to answer that question confidently because the same group of participants also determined similar properties on a range of foods including several cheese types from Italy and the UK. The results for one of these cheeses were so close within the group of labs that such agreement could only have arisen from a truly uniform material tested by truly equivalent experimenters. It is only necessary for a group to agree in *one* calibration exercise for it to be confirmed as 'calibrated'. In this case the real food was more uniform than the 'model' standard material!

The intention was that after 'calibration' the participants would share between them the task of measuring a range of foods within their particular field of interest, and so jointly accumulate ppfs data at a rate proportional to the number taking part. In fact, although this was done to some extent, the 'calibration' stages took very much longer than expected, occupying a large fraction of the 3 years and so, once again, the determination of numerical information on ppfs was, as in COST 90, less than had been hoped for.

WHAT COST 90bis ACHIEVED

Those closely involved in a project are unlikely to be in the best position to make a balanced assessment of its successes and failures, and yet an

'internal audit' is nevertheless necessary, at least as a contribution to the overall process of evaluation.

Cooperation

As in COST 90, most participants in COST 90bis have expressed appreciation of the opportunity to meet, get to know and work jointly with colleagues in similar fields in other European countries. This was felt to be of value both at the time and for the future. Most participants also learned more about their subject and acquired more information on ppfs. They were also alerted to work-in-progress in other countries and indeed in their own, of which they were previously unaware.

Calibration

This, as discussed earlier, is both an essential prerequisite and a source of considerable reassurance to the 'calibrated' participants themselves and to those using their results. It is now known that 'standard' gels made up by individual laboratories cannot be *relied* upon to possess identical mechanical properties. It was also established that it is extremely difficult to find a suitable 'calibration' material/system for diffusivity determinations based on drying. Gels and similar model materials, like most foods, shrink and distort on dehydration, making accurate calculation of diffusivity impossible. A saturated bed of glass microspheres retains its integrity on drying but in no way resembles a food material in its behaviour. Nevertheless, it *was* probably the best choice for 'calibration' purposes. Gels did prove satisfactory as 'calibration' materials for solute diffusivity and dielectric property determination although the latter 'calibration' exercise was not entirely satisfactory because of the widely different frequency ranges of the equipment available in participating laboratories.

The Optical Properties Subgroup colour 'calibration' activities revealed a number of potential sources of error or of differences in results. There was good agreement when measuring standard (Swedish) colour cards of different hue, saturation and brightness, and these results are fully detailed in other chapters. There was also fair agreement on measuring the colour of samples of tomato paste heat-processed (by Londreco, UK) to produce different degrees of colour degradation and distributed in cans to participants, although some refinement in the standard measuring technique was consequently found desirable. Not surprisingly, there was closer agreement between participants when the tomato paste samples were measured using the colour card closely resembling tomato paste as the reference standard than when using the normal black and white reference standards of the

participants' colorimeters. Translucency as an attribute and as a complication in colour measurement was studied and the effects of area of illumination and instrument aperture size were found to be important and were quantified. The suggestion that a range of reference standard 'COST 90' food colour tiles be produced met with wide support within and outside the participating organisations and has been actively pursued, priority being given to the manufacture of a tomato paste colour tile.

For the first time in the near-decade of COST ppfs work a start was made on the organised compilation of a range of comprehensive bibliographies on selected properties. The first of these was published in 1985 (Wolf *et al.*, 1985) on Sorption Isotherms and Water Activity of Food Materials. The next, on Diffusion of Salt in Foods (Rüegg and Schär, 1985) also lists values of diffusivities extracted from the 200 or so references included. Not all participants displayed enthusiasm for the task of compiling and analysing bibliographies in this way, but a small, dedicated group in each subject worked long and effectively to produce further bibliographies on mechanical (esp. B. McKenna and K. Thomas), dielectric and optical/colour (M. Kent and K. Thomas), and diffusional (esp. A. Voilley, D. Vidal and K. Thomas) properties of foods which it is intended to publish as soon as possible in some suitable form. Prior to the actual bibliographic compilations and classifications, alternative systems for their presentation and analysis were studied. The object was to produce data collections of maximum value and convenience. Every effort should be made to complete this important part of 'COST 90bis' work and to ensure that it is kept up to date in the future.

Context

COST 90bis revealed still further the importance of context in relation to ppfs. In most practical situations in which ppfs information is of significance, the numerical value of the property of interest cannot be assumed to be independent of its circumstances. A good illustration is the *viscosity* of food liquids. 'Viscosity' is a *property* whereby liquids continuously resist continuous shear. In Newtonian liquids the magnitude of this shear resistance, τ , is directly proportional to the magnitude of the shear rate, $\dot{\gamma}$; $\tau = \eta\dot{\gamma}$. The constant of proportionality, η , the *coefficient* of viscosity, characterises the 'amount' of viscosity displayed by a Newtonian liquid and its numerical value remains the same whatever the shear rate. It is not the same at different temperatures, however, and so the temperature must always be specified when the value of a Newtonian coefficient of viscosity is quoted. Temperature here is a contextual factor of great importance to Newtonian coefficients of viscosity.

Most food liquids are not Newtonian, however; their shear resistance is not directly proportional to the applied shear rate and so there is no *constant* of proportionality, η , and such liquids do not have a constant 'coefficient of viscosity'. Furthermore, the way in which the shear resistance changes with shear rate may differ in different non-Newtonian liquids so that in some the resistance at high shear rates is less than proportional to that at low shear rates and in others it is more than proportional. There are various ways of expressing this mathematically and even ways of quantifying so-called 'apparent coefficients of viscosity' (not 'apparent viscosity'—that is real enough!) but the value of such a quantity to describe the shear rate response to different shear stresses is largely illusory—and can be positively dangerous in the wrong hands—when it itself changes with the shear *context*. In such food liquids the temperature and the shear conditions are essential *contextual* factors in any quantification of the viscous behaviour of the liquids.

And so it is with most ppfs—to such an extent that published numerical ppfs data may be useless in circumstances in which the same contextual factors are not present. It is apparent as a result of the work of COST 90bis that differences in numerical values for nominally the same ppfs are as likely to be due to unobserved or unrecorded contextual differences as to actual differences in the property or to simple errors in measurement. The example of the mechanical properties of the 'standard' gel referred to earlier is a case in point. By the end of COST 90 the dilemma of how to decide whether differences between measured values were real or apparent (i.e. due to *measurement* differences) had been resolved in principle by the use of 'calibrated' collaboration which was accordingly used extensively in COST 90bis. By the end of COST 90bis the additional consideration of the effect of *context* is seen to be of primary importance in affecting the true value of the property itself, the 'apparent' value obtained by experiment, and the *use* of the value in relation to some practical application. At all three points the contextual effects must be (a) identical, *or* (b) negligible, *or* (c) quantified and compensated for—or a combination thereof. For this reason, the contextual aspects of ppfs should be a primary consideration in any further work in this field.

THE SHORTFALL

If it is true that more is learned from failures than from successes then it is desirable to identify the respects in which COST 90bis did not achieve its goals. These might include the following.

Quantity

No doubt due to features inherent in voluntary international cooperation, the progress made by the Project is less than those involved would have liked. Whether it is in the circumstances less than could reasonably be expected is difficult to say: in the case of COST 90 the better perspective possible a year or two after its termination generally improved the view of its achievements. Certainly the extra year spent on COST 90 affairs at the beginning of the present Project was of value in enabling loose ends to be gathered up and the work brought to a tidier finish. COST 90bis also has ended with unfinished business; some is specific and modest such as incomplete bibliographic tasks. These would benefit from an extra year (now provided—Ed.) such as COST 90 received from the present Project and could be expected to be finished off within such a time scale. Other tasks such as the creation of a set of standard food colour tiles would require longer and will, it is hoped, be pursued by whatever means can be found beyond COST 90bis. (The Community Bureau of Reference is doing so—Ed.)

Participation

Despite what seemed more than adequate publicity by the Project office-holders and others involved, there were too many occasions on which potential participants—individual and institutional—were found in total ignorance of the Project and its direct relevance to their interests too late for them to take effective part. There was evidently a shortfall in the extent to which some Participating State Representatives had succeeded in informing all potential contributors/beneficiaries in their countries. Any future projects should take greater care to ensure that *all* those who *might* be useful participants are fully informed at the beginning.

Intranational Support

It has seemed on occasions that communication and support from those responsible for a country's primary decision to participate to those required to implement it—notably some subject subgroup participants—has left something to be desired. Some of those doing the actual work have had to struggle to find the modest resources necessary to support their efforts to represent their country adequately in the Project. Enthusiasts in that position 'soldiered on' largely on their own personal or departmental resources whereas others have had to withdraw for lack of resources rather than lack of relevance or interest. It has been a period of increasing economic stringency in Europe and circumstances do change after

decisions are made, but it would be better for all concerned if, having willed the ends, at a national level, Participating States would either will the means and see to it that their country's team was properly resourced to participate or, if later prevented by national circumstances from doing so, would ensure that their national CCCC Representative informs the Project Management *and* their own subject participants of the changed circumstances promptly and fully.

CONCLUSION

The first task of management, it is said, is to organise its succession. COST 90bis has attempted to do this by a further COST 90-type action either independently or as part of the Umbrella Programme on Food Technology and Science (see Chapter 44).

COST 90bis should be, and, historically, doubtless will be, seen as a part of an on-going process of cooperation in Europe and further afield in the important subject of physical properties of foods. In promoting both international cooperation and the subject of ppfs it will undoubtedly be seen to have been a Good Thing!

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Part 1
DIFFUSION

2

Diffusion in Foods: The Work of COST 90bis Subgroup

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SUMMARY

The work of the Diffusion Subgroup of COST 90bis is outlined and the reasons for undertaking such a project are discussed.

The very idea of mass diffusion in foods should be handled with extreme care: the exchange of information about diffusion should be preceded by a careful definition of any given constitutive equation. Moreover, there is no 'pure experiment' in the field of diffusion: all real measurements of diffusion coefficients are influenced by other interfering phenomena.

Two techniques have been explored by the group: diffusion of solutes in water contained in gels and drying experiments. In addition to acquiring more data, the subgroup has evaluated the methodologies in current use and progress has been made in experimental techniques.

NOMENCLATURE

D_{AB}	binary material diffusivity based on Fick's law
D_A^{eff}	effective diffusivity of species A in complex body
D_{AB}^m	multicomponent binary diffusivity
D_{Am}	multicomponent diffusivity of A in mixture m
D_{AB}^T	activity-corrected diffusivity
D^T	material diffusivity induced by temperature gradient
D_{LT}	liquid diffusivity induced by temperature gradient in porous bodies
log	natural logarithm
M	molar mass
R	gas constant

\bar{V}	partial molar volume
a	activity
c	total molar concentration
g	force acting on unit mass of a given species (vector)
k	relative permeability
n	mass flux (vector)
p	total pressure
x	molar fraction
w	subscript for water
ν	kinematic viscosity
ρ	total mass concentration
ω	mass fraction
ψ_c	capillary potential
∇	nabla

INTRODUCTION

The need for producing and collecting data in the field of physical properties of food is the primary motivation of both the COST 90 and 90bis Projects.¹ Material diffusion is important in at least three fields of food conversion: introduction or removal of solutes (as in preservation and cheese making), drying and aroma retention. Such a property can be used in the same way as other physical data for design purposes by engineers; in this case its reliability is essential. The food scientist is also interested in diffusivity in order to understand the influence of storage and preservation on food quality. Finally, and this appeared to be essential to the members of the subgroup, accurate data on simple systems are necessary for incorporation into models for the prediction of diffusivities in more complex systems, whereas measurements of so-called 'effective diffusivities' (Rotstein²) for complicated situations serve to validate the models.

During the course of a European project characterised by Concerted Action a compromise must be found between desirably elevated scientific goals and the availability of the time and resources of the participants, bearing in mind the need for compatibility between the common objectives and the separate individual projects of the participants in the group. Fortunately, important amongst the objectives of COST Projects are first the necessity to agree on clear concepts and to speak the same scientific language, and secondly the urge to improve the technical expertise of the participating laboratories by mutual help.

The subgroup recognised that there are at least two kinds of diffusivity: true diffusivity for single-phase molecular transport based on Fick's law and effective diffusivities for complex systems. In the literature there are at least three experimental methods to evaluate diffusivity: concentration profile analysis for non-stationary process, drying rate measurement, and sorption and desorption kinetics. The task to investigate all the possible cases would be immense, so the working group decided to concentrate its efforts on methodology aspects and undertook the following tasks:

- (A) Definition of two basic methods; establishment of common experimental procedures.
- (B) Measurement of the true coefficient of diffusion of solutes in water. Evaluation of the method based on concentration profiles in gels.
- (C) Application of the above method to the diffusion of salt in cheese and of volatiles in water in the presence of a third compound.
- (D) Measurement of an effective water diffusivity (similar to an internal mass transfer coefficient) by means of a drying experiment. Definition of a model system for a collaborative study. Analysis of the results in terms of method and experimental difficulties.
- (E) Application of the above method to the study of the diffusion of water in dimensionally unstable gels.
- (F) Compilation of references to relevant literature (water and solute diffusion, drying characteristics).

The detailed results of the various tasks undertaken are given in separate papers. This paper outlines the general framework of research in the field of material diffusion in order to place the work of the subgroup in context.

THE USE AND MISUSE OF THE CONCEPT OF DIFFUSION

As far as transport properties are concerned food materials can be classified into three groups according to various authors.^{3,4}

Group I—Liquids, solutions and gels (e.g. milk, fruit juices, gelled products).

Group II—Dimensionally stable capillary-porous and hygroscopic-porous materials (e.g. packed beds of corn; cf. also wet sand, soils).

Group III—Dimensionally unstable capillary-porous and hygroscopic-porous deformable materials. These materials have a matrix of a colloidal nature, exhibit shrinkage and may develop a pore structure during drying (e.g. vegetables, meat, etc.).

Note that any one actual food can contain parts belonging to more than one of these groups.

Single-phase Diffusion

The concept of diffusion originated from the observation that any particular component in a single-phase system can move and be redistributed in the absence of any external mechanical or physical constraint or pressure gradient. This property is linked to random molecular movement leading to the perpetual exchange of momentum between atoms or molecules at any temperature. This random movement is responsible for the disappearance of spontaneous fluctuations in density or composition.

From any uneven initial distribution of its components an isolated system will change towards uniformity of distribution of the various components; this fact is expressed by the second law of thermodynamics. This type of phenomenon is an irreversible process leading to the isolated system's maximum entropy.⁵

It is then clear that such a phenomenon can be encountered only in very simple food materials: generally speaking, only in foods of Group I can the concept of diffusion be applied strictly. In more complex situations, the diffusion law should be applied separately to each of the phases present (e.g. cell membranes, vacuoles, internal gas phase, etc.). The next task is then the difficult one of constructing an overall mass transport property for the whole from the various contributions.²

For the correct use of diffusivities in single phases, distinction must be made between the various definitions. For binary systems, the mass flux, n_A , with respect to stationary coordinates is

$$n_A = -\rho D_{AB} \nabla \omega_A + \omega_A (n_A + n_B) \quad (1)$$

where D_{AB} is a mutual diffusion coefficient based on Fick's law.

Modern theories have postulated that the gradient of chemical potential at constant temperature is the true generalised force which causes diffusion. As chemical potential is linked to activity a , eqn. (1) may be transformed into

$$n_A = -\rho D_{AB} \left[\frac{\partial \log a_A}{\partial \log x_A} \right]_{T,p} \nabla \omega_A + \omega_A (n_A + n_B) \quad (2)$$

Comparison of these two equations shows that an activity corrected diffusion coefficient, D_{AB} , can be defined in the form

$$D_{AB} = D_{AB} \left[\frac{\partial \log a_A}{\partial \log x_A} \right]_{T,p} \quad (3)$$

These two coefficients are identical for ideal solutions where activity is simply proportional to mole fraction x_A .

If careful experiments are performed it is generally possible to find a value for D_{AB} through (1), but the fact that D_{AB} is more concentration-dependent than D_{AB} in the liquid phase⁷ has led some authors to use the latter as a basic constant value and to derive through eqn. (3) a concentration dependence function.²

Still, for binary mixtures great care must be taken when performing experiments to allow for any mass fluxes induced by other physical forces. Three secondary mass flux contributions may be added to n_A in eqn. (1):

- (1) A contribution due to thermal driving forces; this effect is generally small unless significant thermal gradients are present:

$$-D_A^T = \nabla \log T \quad (4)$$

where D_A^T is the thermal diffusion coefficient.

- (2) A contribution due to pressure gradients; this pressure diffusion is different from bulk flow:

$$-c D_{AB} \frac{M_A M_B}{RT} \omega_A \left(\frac{\bar{V}_A}{M_A} - \frac{1}{\rho} \right) \nabla p \quad (5)$$

- (3) Finally, a forced diffusion contribution due to any external forces acting on a given species which for example carries an electric charge:

$$-c D_{AB} \frac{M_A M_B}{RT} \omega_A \omega_B (\mathbf{g}_A - \mathbf{g}_B) \quad (6)$$

where vector \mathbf{g} represents the force per unit mass exerted on a given species. Transport described by eqns. (4) and (6) are usually negligible.

For a multicomponent mixture, eqns. (4), (5) and (6) can be extended.⁸ The major difficulty lies in the fact that D_{AB}^m , the value of the diffusivity of the pair A-B in a multicomponent mixture, is different from the value of D_{AB} in a binary system. A relationship can be derived to express multicomponent diffusivities in terms of binary diffusivities for ideal solutions.⁸ Unfortunately very little attention has been paid by experimenters to such subtleties and the diffusion coefficients that appear in the literature for such cases are generally ill-defined. At best, results are given in the form of binary-like effective diffusivities, i.e. diffusion of species A in the mixture considered as the second species.

Multiphase Effective Diffusivities

When the system is composed of several phases, generally liquid and gas in a solid matrix, true diffusion phenomena can take place in these phases and also other kinds of mean transport. For the former, the above-mentioned theories may be used but not for the latter.

(a) The only transport phenomena which can reasonably be described by diffusion are those where random molecular motion is the cause of the movement of a particular component. In the separate regions of one food material, gas diffusion and liquid diffusion may occur, for which eqn. (1) is applicable. A common example is Stephan flow in the gas phase where only one species is considered as moving, the second one being considered as stagnant; application of eqn. (1) gives the mass flux as

$$-\rho D_{AB} \frac{1}{\omega_B} \nabla \omega_A \quad (7)$$

Two particular cases are also to be considered: Knudsen diffusion and surface diffusion. When the scale of observation, i.e. the average diameter of the pores, is smaller than the mean free path of the molecules, the cause of redistribution of the various molecules is no longer simply the intermolecular collisions but also collisions with capillary walls: the driving force is still the same as in normal diffusion but the diffusion coefficient is specific to each situation. Two-dimensional interdiffusion of adsorbed molecules is treated in just the same way as the normal case; the corresponding fluxes are generally small.

Unlike simple single-phase situations, these simple phenomena do not extend to large regions of the material; on the contrary, they are confined to small constituent parts; even so, the shape of the domains of pure diffusion are complex. To overcome this problem, use is made of a structural factor which modifies the basic diffusion coefficient: this factor normally includes the volume fraction of the particular phase and tortuosity. Further, the architecture or relationships of the constituent parts is taken into account by means of a series or parallel or hybrid model in the same way that heat conductivity is treated. These two refinements provide what is commonly accepted as an effective diffusivity: D^{eff} ; as it is without any physical sense in terms of diffusion to define a single barycenter for all phases the total mass flow is expressed as

$$\mathbf{n}_A = -D_A^{eff} \bar{\rho} \nabla \bar{\omega}_A \quad (8)$$

The quantities $\bar{\rho}$ and $\bar{\omega}_A$ are weighted mean values for ρ and ω_A for the various phases. The calculations of these average values are obtained either

by simple combination (Luikov⁹) or by volume averaging techniques (Whitaker¹⁰).

If the experiments to evaluate effective diffusivity according to eqn. (8) are designed such that no other interfering phenomena can occur, then the use of the term 'diffusion' is legitimate. However, it is very difficult to avoid any temperature or total pressure gradients: the first one will provoke thermal diffusion in each phase and the second viscous flow (filtration). Any use of the term diffusion in the latter case is incorrect.

(b) Another flow which is incorrectly referred to as diffusion is capillary flow. Here the forces in question have their origin at the interface of the phases and are true macro-mechanical forces. Water flow in capillary-porous bodies is the commonest example; it is very common during drying and the mass fluxes involved are usually important because of the density of liquid water. Furthermore, all the solutes in water are carried along simultaneously. Traditionally but wrongly, the term 'capillary diffusion' is used for this bulk flow induced by surface tension. Darcy's law describes the movement of water with respect to stationary coordinates. If a local capillary potential, ψ_c , is defined which is linked to the radii of curvature of the menisci, the mass flux is

$$\mathbf{n}_{LW} = -\frac{k_L}{v_{LW}} \nabla \psi_c \quad (9)$$

The relative liquid permeability, k_L , is basically a geometrical structural factor for a given liquid moisture content. If the gradient of capillary potential is changed into that of liquid water average mass fraction $\bar{\omega}_{LW}$ multiplied by the partial derivative $\partial\psi_c/\partial\bar{\omega}_{LM}$ and a contribution from the thermal gradient is added, eqn. (9) becomes

$$\mathbf{n}_{LV} = -\rho [D_{L\text{cap}} \nabla \bar{\omega}_{LW} + D_{L,T} \nabla T]$$

It should be noted that although the thermal gradient diffusivity, $D_{L,T}$, appears like a cross-term of linear irreversible thermodynamics, it is fundamentally different from D_A^T in eqn. (4), which is a true Soret effect. Here $D_{L,T}$ can be simply related to the changes in surface tension with temperature and to the relative permeability.¹¹

When water is bound to a surface in the hygroscopic state it can move under the influence of a surface pressure gradient. As for capillary pressure this gradient is linked to the equation of state, namely the adsorption isotherm. Such a movement should be referred to as surface flow rather than surface diffusion.

Returning to the classification of food products set out in the

Introduction, it can be said that true diffusion is responsible for mass transfer in hygroscopic-porous and non-porous foods in the absence of total pressure gradients. On the other hand, capillary-porous products may exhibit a behaviour in which mass transport is due partly to mechanical viscous flow rather than diffusion even under isobaric and isothermal conditions.

QUESTIONS

Having set the scene, the question faced by the subgroup was the choice of its line of research. To make the maximum advantage of international collaboration the emphasis had to be on experimentation rather than on theoretical investigations. From what has been said previously, it is obvious that not only the methods of measurement but also the properties to be measured are not simple and straightforward. The following list of questions about diffusion in foods is not complete but gives an idea of the current trends in the field. With five categories and subcategories of food and three techniques of measurement there are some twelve practical cases. For each of these cases the questions are:

- (i) The technical qualities of the experimental arrangements necessary to obtain valid results.
- (ii) The route for extracting the diffusion coefficient from the experimental data.
- (iii) Any numerical problems related to the processing of raw data.

Broader questions still open for further reflection are:

- (iv) The physical significance of the measured quantity.
- (v) The importance of secondary effects (thermal gradient diffusion, etc.).
- (vi) The prediction of complex diffusivities from simple properties.
- (vii) Conditions for utilisation of diffusion data for engineering purposes.

The subgroup decided to contribute to the solution of questions (i), (ii) and (iv), and undertook the tasks as defined in the Introduction.

PARTICIPATION

The first meeting of the subgroup on diffusion properties was held in Dublin in September 1983. Concrete action started in February 1984 and

TABLE 1
LIST OF PARTICIPATING INSTITUTIONS

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- (1) Food Preservation Laboratory, Catholic University of Leuven, Belgium
 - (2) Food and Chemical Industries Research Training Centre (CERIA)—Analytical and Test Station, Brussels, Belgium
 - (3) Federal Dairy Research Institute, Liebefeld-Bern, Switzerland
 - (4) Department of Food Technology, Danish Technical University, Lyngby, Denmark
 - (5) Higher National College for Agronomy and Food Industries (ENSAIA), National Polytechnical Institute of Lorraine, Nancy, France
 - (6) Higher National College for the Chemical Industries (ENSIC), National Polytechnical Institute of Lorraine, Nancy, France
 - (7) Higher National College of Metallurgy and the Mining Industry (ENSMIM), National Polytechnical Institute of Lorraine, Nancy, France
 - (8) Higher National College of Biology Applied to Nutrition and Food (ENSBANA), University of Burgundy, Dijon, France
 - (9) Laboratory of Biochemical Engineering, University of Clermont II, France
 - (10) Laboratory of Biochemistry and Food Technology, Languedoc University of Science and Technology, Montpellier, France
 - (11) Department of Chemical Engineering, National Technical University, Athens, Greece
 - (12) Federal Research Institute of Nutrition, Karlsruhe, Federal Republic of Germany
 - (13) Ministry of Agriculture, Fisheries and Food, London, UK
 - (14) Polytechnic of the South Bank, London, UK
 - (15) Experimental Station for the Food Preservation Industry, Parma, Italy
 - (16) Department of Dairy and Food Engineering, University College, Cork, Eire
 - (17) Department of Food Science, Biotechnology Agricultural University, Wageningen, The Netherlands
 - (18) Department of Agricultural and Food Industries, Polytechnical University of Valencia, Spain
 - (19) Department of Food Engineering, University of Lund, Sweden
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TABLE 2
CONTRIBUTIONS OF THE DIFFERENT PARTICIPANTS

Task	Institutions																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
A. Definition of work	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
B. Solute diffusion in water/gel system	x			x			x	x	x						x				
C. Solute diffusion in foods			x						x		x	x							
D. Collaborative study on drying	x			x		x				x	x				x	x	x	x	
E. Drying of gels	x	x	x	x		x	x		x		x				x	x	x	x	
F. Compilation of literature								x	x		x	x	x			x	x		

ended in August 1986. During this rather short period 16 laboratories carried out experiments on existing equipment or on new devices for the purpose and 19 laboratories in all participated in the programme. Table 1 shows the names of the participating institutions. There is no doubt about the success of the participation because a number of new laboratories took part (e.g. from Spain and France). Table 2 summarises the input by the various contributors.

QUALITATIVE RESULTS

Too many uncertainties were associated with the accuracy and the significance of experimental measurement of diffusion coefficients for the group to start directly in disperse order to measure those properties on real foods. So, during the definition phase of the work it was decided to concentrate on two systems with two methods.

The group selected gels made from agarose of analytical grade for the determination of solute diffusivities by the Naesens method (concentration profile analysis) and for the drying of a dimensionally unstable food model. Additionally, some members of the group used agar-agar or gelatine for preliminary experiments. For the collaborative drying experiment the choice was for glass microspheres from a common source. These glass spheres were to be saturated with water and contained in shallow dishes in order to produce a model capillary-porous body.

The sodium chloride diffusivity was measured for different concentrations: the method of contact of the two cylinders of gelled water proved to be adequate and accurate. The material involved and the analysis technique are not too sophisticated and many laboratories working in food science or engineering could adopt this method. In particular, salting and curing processes can be examined in this way. There is no doubt that coefficients of diffusion obtained by this method are highly significant; the sodium concentrations which were used (0–5%) correspond to nearly ideal situations; the water and the second solute are stationary, and there is no appreciable bulk flow. The two specific papers which present the detailed results of the COST 90bis work are Chapters 7 and 8. In addition, work on the migration of solutes during blanching and on the salting of olives in brine were undertaken respectively by laboratories 12 and 11 and are the subject of separate contributions.

Diffusivities derived from drying experiments are much more questionable. Firstly because foods and food-like substances can be heterogeneous

and secondly because the phenomena involved in drying experiments are never purely diffusive. The subgroup first agreed on a collaborative experiment designed to test the reproducibility between the different experimental centres and the numerical problems associated with the analysis of the raw data. Beds of glass microspheres filled with water are not, by any means, food-like substances but were chosen deliberately as reproducible material suitable for testing the performance of experimental rigs and expertise.

The information concerning internal movement of moisture in the bed is contained in the falling-rate period of drying; because this period was rather short in the case of these glass spheres much caution should be exercised in the experiment itself. In particular, continuous recording of the weight of the sample is advisable. As a drying curve represents the drying rate versus moisture content, the raw data of weight versus time have to be transformed. It is recommended that this transformation be made automatically by microcomputer; it has been recognised by the group that, although popular, the drying method can be rather expensive if reasonable accuracy is sought.

The determination of a diffusion coefficient from the falling-rate period of drying was not the purpose of the exercise; the mechanisms of movement of water are far too unlike simple diffusion, involving capillary flow, evaporation and vapour diffusion from a receding front. But as the falling-rate regime is almost linear the group used it to standardise the method for determining critical moisture content and the most probable rate of drying in the first period. Of the three methods considered, the analysis of the curve, weight versus time, which was represented by a linear and an exponential section, gave the best results. Ninety-one experiments carried out in six laboratories confirmed that the 95% confidence interval for mean value cannot be less than $\pm 0.3 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$.

The work on the drying of dimensionally unstable material such as agarose gel and gelatine approached the case involving a diffusion coefficient which varies with moisture content. Drying curves show a convex-upward part during the falling-rate regime. Two methods of analysis were considered: the regular regime method (Schoeber¹²) when all drying curves merge into one irrespective of initial conditions and the solution of the partial differential equations corresponding to heat and mass micro balances in a moving frame of reference; the programme for the first method was made available to all by the Wageningen group. The first experiments also led participants to define the experimental conditions more explicitly.

Finally, one of the outputs of the group was to gather more than 400 references on water transport in food and related substances and about 100 on salt diffusion. This contribution has been amalgamated with the results of the Data group and reprocessed.

CONCLUSIONS

Mass transport properties are never easy to measure, especially in foods. Pure diffusion rarely occurs alone; more often different diffusivities for each part of the product have to be combined. Capillary flow is frequently but incorrectly treated as diffusion. For engineering purposes an effective overall diffusivity can be a useful property.

The evaluation of the diffusivity of solutes in 'gelled water' has been developed and the experimental details and the mathematical treatment clarified.

In the case of drying rate measurements, some technical progress has been made in relation to the specifications of equipment and to the techniques for analysing the results.

The results obtained in future by the procedures developed in COST 90bis should be more accurate and more significant. From now on communication between participants should be more efficient. Any exchange of information on a physical property depends on the precision of the definitions and on the reliability of results; the COST 90bis Subgroup on 'Diffusion' has clearly contributed to both aspects.

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A Collaborative Experiment on Drying Beds of Glass Spheres

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SUMMARY

It is possible to derive diffusion coefficients from drying experiments. This method is analysed with respect to theoretical fundamentals, experimental procedure and mathematical treatment. In COST 90bis, six laboratories participated in a collaborative calibration experiment involving the drying of beds of glass microspheres. The technical features of the experimental equipment are assessed and simple rules for the determination of an effective diffusivity are proposed. Possible causes for differences between laboratories are discussed.

NOMENCLATURE

D	diffusivity ($\text{m}^2 \text{s}^{-1}$)
g	gravity acceleration (m s^{-2})
h	external heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)

<i>l</i>	bed thickness (m)
<i>m</i>	mass (kg)
<i>n</i>	number
<i>r</i>	radius of microsphere (m)
<i>t</i>	time (s)
<i>T</i>	temperature (K)
<i>u</i>	velocity (m s^{-1})
<i>V</i>	drying rate ($\% \text{s}^{-1}$)
<i>X</i>	moisture content; w/w, dry basis (%)
ϕ	relative humidity of air (%)
λ	heat conductivity of the bed ($\text{W m}^{-1} \text{K}^{-1}$)
∇	nabla operator
ρ	density (kg m^{-3})
σ	water surface tension (N m^{-1})

Subscripts

i	initial
I	first period
cr	critical
eff	effective
eq	equilibrium
L	liquid
s	solid
V.	vapour
1, 2, 3	first, second and third method (of determination of D)

INTRODUCTION

For the optimal control of drying processes of any particular material, or for any precalculations for drying processes, a mathematical description of individual stages taking place during drying, and the combination of these, are of considerable value. A comprehensive description is very difficult or even impossible because of a lack of data on materials, so simple models which allow the drying process to be estimated approximately are frequently used in practice. A particular simple model which is frequently described in the literature and often used in practice is an apparent diffusion model to describe mass transport during the falling-rate period of drying.² Although this model—and hence its validity—is based on several

simplifying assumptions, the question arises as to whether it may be successfully referred to systems which fulfil only some of these preconditions and, furthermore, when the objective is rather to obtain average moisture content value versus time than to determine the moisture content profile inside the porous medium during drying.

One of the tasks of the COST 90bis programme, therefore, was to determine apparent diffusion coefficients for water in simple model systems, with the aim of establishing guidelines for other drying experiments and of determining the reproducibility of the measurements for a simple system (glass microspheres/water) as between the different participants.

THEORETICAL BACKGROUND

Drying experiments are frequently used to evaluate mass transport properties in solids, gels and liquids. If a wet sample is exposed to constant convective conditions, two regimes may be observed for the drying rate:

- During the first period, the drying rate ($-d\bar{X}/dt_1 = V_1$) remains reasonably constant. The observed water flux from the sample is controlled by the external conditions (temperature T , air velocity u and relative humidity ϕ). The internal mechanisms for water transport within the material are sufficient to supply liquid water to the surface of the solid so that these mechanisms do not influence the drying rate during this period.
- During the second period, which begins at an average 'critical' moisture content \bar{X}_{cr} , the drying rate decreases: the internal transfer of liquid water and vapour becomes the regulating process. It can even be possible to distinguish between two falling-rate periods, the first corresponding to a positive value for the rate at the final moisture content, the latter corresponding to an asymptotic approach to a zero final rate of drying at the equilibrium moisture content (Fig. 1). Only analysis of this second type of falling-rate period will enable quantification of internal transport properties.

Internal Mechanisms of Transport

A vast literature pertaining not only to food engineering but also to chemical and geological engineering deals with internal transport in porous

materials.^{3,4,6} The following internal phenomena are involved (see Chapter 2).

- Liquid flow induced by the capillary pressure gradients as shown in Chapter 2; these gradients have their origin in the differences of water content and temperature. External forces such as gravity may also influence liquid flow.
- Vapour flow in the gas phase induced by the partial pressure gradients also caused by differences in water content and in temperature.

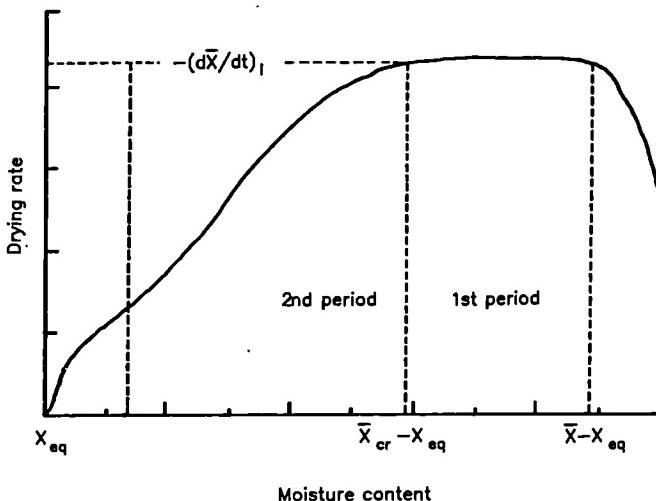


Fig. 1. Typical drying-rate curve.

In the case of drying glass microsphere beds, the temperature conditions are uniform enough to permit any filtration process. As the capillary effects dominate the effects of gravity, the latter are neglected; for a bead radius r of $50\text{ }\mu\text{m}$ and a bed thickness l of 10 mm , the value of $(2\sigma/r)/\rho_L g l$ is around 30. This is not sufficient in fact to neglect gravity, but it is nevertheless assumed that gravity does not affect the drying kinetics in the falling-rate period. Further, drying can be considered as an isothermal process because the thermal Biot number $h l / \lambda$ is near 0.2.

Description of Drying by Effective Diffusivity

With the above simplifying assumptions the local internal mass transport equation is

$$\frac{\partial X}{\partial t} = \nabla[(D_L^{\text{eff}} + D_V^{\text{eff}})\nabla X] \quad (1)$$

The effective diffusivities which already include the structural factors (Chapter 2) become preponderant in specific cases: liquid diffusivity in the capillary region and vapour diffusivity in the hygroscopic region. In any case these properties vary greatly with water moisture content.

Solution of eqn. (1) leads to the moisture profile for a given set of boundary and initial conditions. However, the aim of this study is much more practical; only the average moisture content is required in many cases. Considering two diffusivities as a function of moisture content would result in very time-consuming and cumbersome experimental work; if average values are sufficient to combine the two phenomena into one single constant, apparent diffusivity D could be attempted:

$$\frac{\partial X}{\partial t} = D \nabla^2 X \quad (2)$$

Although widely used for the sake of simplicity, eqn. (2) involves several unrealistic assumptions. The limitations of diffusion equation (2) for such cases have been well known since the pioneering work of Geaglske and Hougen¹ in 1937.

Determination of an Apparent Diffusion Coefficient

The mathematical solution of even eqn. (2) is not as straightforward as it appears. It should be used during the second phase of drying with the initial conditions those at the end of the first phase. Because glass beads are non-hygroscopic, the boundary condition corresponds to zero surface moisture content ($X_{\text{eq}} = 0$). The situation would be more complicated in the case of a non-degenerate sorption isotherm. It is commonly assumed that at the beginning of the second phase moisture is evenly distributed ($\bar{X} = \bar{X}_{\text{cr}}$); the solution is then well known:

$$\frac{\bar{X} - X_{\text{eq}}}{\bar{X}_{\text{cr}} - X_{\text{eq}}} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \frac{-(2n+1)^2 \pi^2 D t}{4l^2} \quad (3)$$

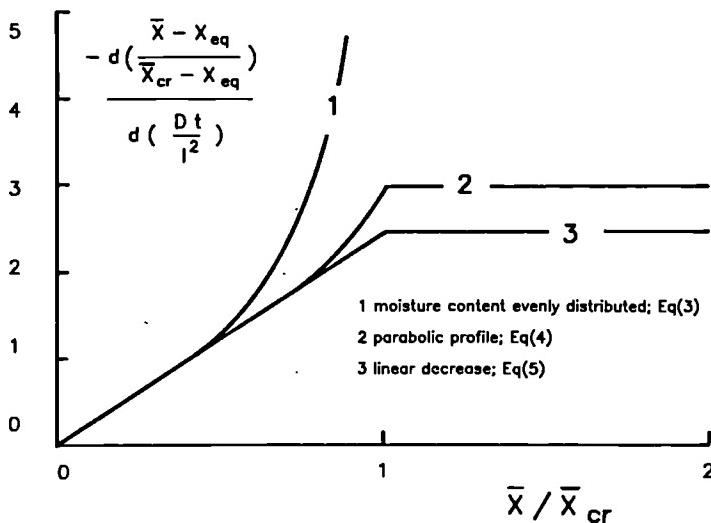


Fig. 2. Various forms of the drying-rate curve.

It is strange to see that the graph of

$$-\frac{d\left(\frac{\bar{X} - X_{eq}}{\bar{X}_{cr} - X_{eq}}\right)}{d\left(\frac{Dt}{l^2}\right)}$$

derived from eqn. (3) is not a straight line, although it is taken for granted to be by many authors (Fig. 2). Actually, to avoid this paradox, only the first term in the series in eqn. (3) is used.

It is more elegant to describe the initial condition as a quasistationary profile for moisture content in the case of a constant mass flux at the surface. This corresponds to a parabolic profile. The exact solution is then

$$\frac{\bar{X} - X_{eq}}{\bar{X}_{cr} - X_{eq}} = \frac{96}{\pi^4} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^4} \exp \frac{-(2n+1)^2 \pi^2 Dt}{4l^2} \quad (4)$$

The drying rate deduced from eqn. (4) is shown in Fig. 2. It is reasonable to approximate this rate to a linear decrease, as with the first term of eqn. (3) (with the approximation $96/\pi^4 = 1$):

$$-\frac{d\bar{X}}{dt} = \frac{\pi^2 D}{4l^2} \bar{X} \quad (5)$$

In fact, this behaviour is that of an exponential decrease in the average moisture content, the time constant of which appears as $4l^2/\pi^2D$. Both presentations are equivalent.

In order to calculate a drying time, the drying rate in the first phase, V_1 , has to be evaluated from correlations and the apparent diffusivity, D , must be known. The only requirement for this model to be acceptable is that D should not depend on bed thickness.

AIMS OF THE COLLABORATIVE STUDY

Extraction of an apparent diffusion coefficient from drying curves is widely used. It is then essential to know what credit can be put on the corresponding data in the literature.

For this purpose the subgroup agreed on a collaborative experiment designed to test

- the experimental facilities and their use; and
- the methodology of analysis and the associated numerical problems.

Beds of glass microspheres with the interstices filled with pure water were chosen because this system can be easily reproduced in every laboratory so that the variability of the results can only be attributed to the experimental facilities, the expertise of the operator and the method of analysis of the raw data.

What should have been a first calibration exercise proved to be much more difficult with regard to both experimentation and data processing.

MATERIAL AND EXPERIMENTAL PROCEDURE

Glass Microsphere Beds

The choice of glass microsphere beds originates from the definable nature of the material. This exercise being a calibration operation, reliable reproducibility of the materials was a necessary prerequisite.

The diameter of the glass microspheres was 100 µm. The beads were filled into circular Petri dishes or square Plexiglass boxes (50 × 50 mm) and wetted to saturation with double-distilled water. In order to level the surface the sample was gently tapped, for example, with a rubber-tipped rod. Various bed depths ($2 \leq l \leq 16$ mm) were used. The depth was measured as carefully as possible with a micrometer after drying.

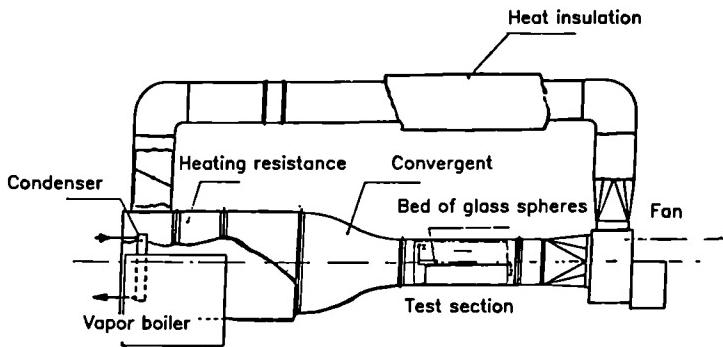


Fig. 3. Typical drying equipment.

Drying Conditions

The specified external conditions were:

- temperature of the bulk drying air $T = 60^\circ\text{C}$
- air velocity $u = 2 \text{ m s}^{-1}$
- air relative humidity $\phi = 40 \text{ or } 60\%$

It should be noted that such aerothermal conditions are not very well defined. For instance, it is possible to put the sample in the bulk air flow or at the wall of the test section. Due to this fact some variations in the constant drying rate were to be expected in the different laboratories.

Drying Equipment

Figure 3 shows a return flow wind-tunnel with carefully regulated air temperature and relative humidity (based on measurement of the dew point) which can be regarded as a typical drying installation.

Sample weight was measured with an electronic balance and recorded continuously. To exclude the influence of aerodynamic noise, an average value at short intervals was used.

As a conclusion at this point, the necessity for very precise and constant drying conditions during the experiments (in spite of the concomitant difficulties) should be emphasised.

EXPERIMENTAL RESULTS

In the collaborative study six laboratories took part, producing altogether the results of 91 drying experiments. The participants were requested to submit raw data so that they could all be treated in the same way (e.g. determination of the endpoint of the drying experiment).

TABLE 1
PARTICIPANTS, NUMBER AND CONDITIONS OF DRYING EXPERIMENTS

<i>Participant^a</i>	<i>Number of experiments</i>	<i>T</i> (°C)	<i>ϕ</i> (%)	<i>u</i> (m s ⁻¹)	<i>l</i> (mm)
Moyné	7	21	60	60	1.5
			60	40	2.0
MacCarthy	16	10	60	6	1.3
			55	26	8
Motarjemi	19	28	60	45	2.0
			60	40	2.0
Poulsen	4	2	60	18	1.8
Raouzeos	11	9	60	35	2.0
			60	58	2.0
			60	45	1.4
Meerdink	17	21	60	60	2.0
					4, 5, 7, 9

^aNumber refers to Table 2 in Chapter 2.

In addition to the fact that, due to technical limitations in some of the experimental equipment, some departures from the specified external drying conditions occurred, a few participants also varied the relative humidity of the air and the thickness of the glass sphere bed systematically in order to examine the influence of these variables (Table 1).

The course of one typical drying experiment is presented in Fig. 4

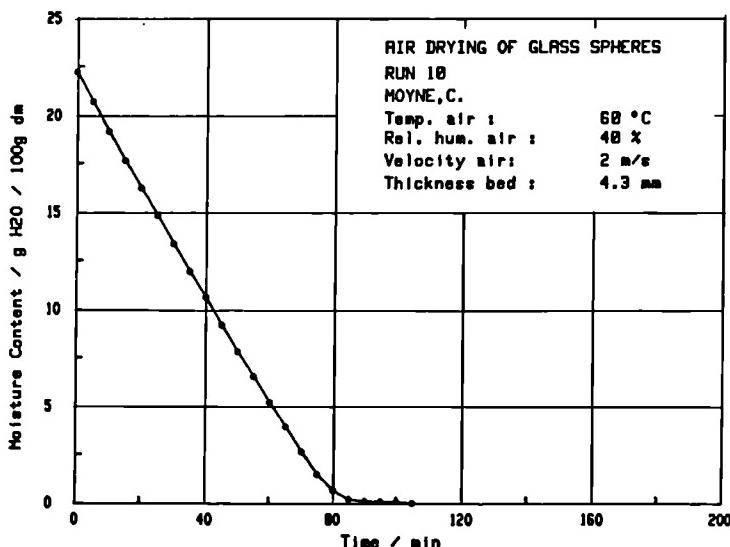


Fig. 4. Experimental drying curve.

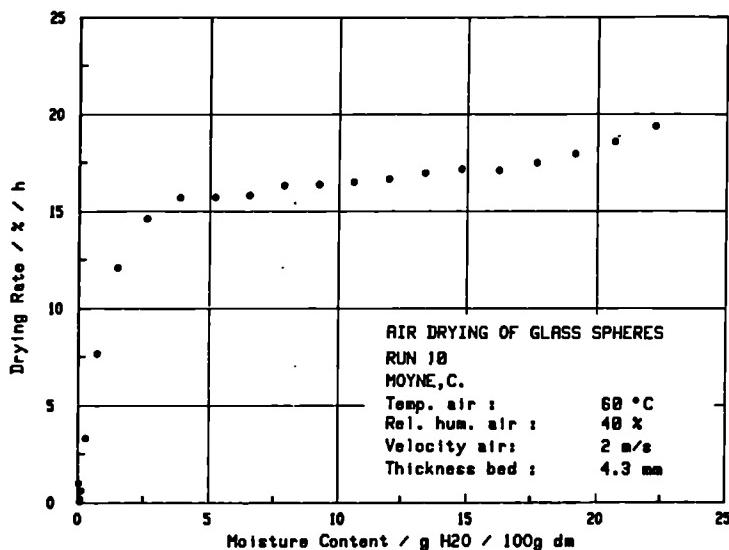


Fig. 5. Experimental drying-rate curve.

(moisture content versus time) and Fig. 5 (drying rate as a function of moisture content). The curves reveal an extended constant-rate period and a very short falling-rate period.

CALCULATION OF APPARENT EFFECTIVE DIFFUSIVITY

Assuming that in the falling-rate period the diffusion law can be applied, taking into account only the first term of the series in eqn. (3) and assuming $X_{eq} = 0$ and $8/\pi^2 = 1$, the solution for the mean water content, \bar{X} , can be expressed as

$$\bar{X} = \bar{X}_{cr} \exp \left[-\frac{\pi^2 D(t - t_{cr})}{4l^2} \right] \quad (6)$$

For the derivation of diffusion coefficients from drying experiments, three different methods have been used.

1. Determination of D from the Drying-rate Curve

Based on eqn. (6), the theoretical drying rate is

$$-\frac{d\bar{X}}{dt} = \frac{\pi^2 D}{4l^2} \bar{X} \quad \text{for } \bar{X} < \bar{X}_{cr} \quad (7)$$

and

$$-\frac{d\bar{X}}{dt} = V_1 = \text{const} \quad \text{for } \bar{X} \geq \bar{X}_{cr} \quad (8)$$

By plotting the theoretical drying rate as a function of \bar{X} (Fig. 6) it becomes evident that the apparent diffusion coefficient can be determined by the relationship

$$D = \frac{4l^2}{\pi^2} \frac{V_1}{\bar{X}_{cr}} \quad (9)$$

To obtain the apparent diffusion coefficients for the 91 drying experiments, the constant drying rate and critical moisture content for each experiment had to be determined. The determination is based on a polynomial regression of the experimental moisture data as a function of time to obtain an explicit expression for the drying curve which could be differentiated

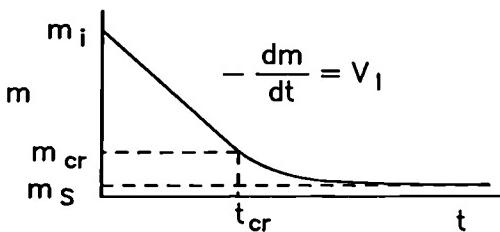


Fig. 6. Idealised drying-rate curve.

leading to the course of the drying rate as a function of moisture content. A special least-squares method was then applied to these data to evaluate the breakpoint of the curve (Fig. 6) and consequently the factors V_1 and \bar{X}_{cr} . The apparent diffusion coefficients D_1 (subscript 1 refers to method 1) of the 91 drying experiments, together with the corresponding critical moisture contents \bar{X}_{cr} , are compiled in Table 3. A listing of the corresponding computer program is given as an appendix.

2. Determination of D from the Drying Curve, mass = f (time)

With the definition of the mean moisture content

$$\bar{X} = \frac{m - m_s}{m_i - m_s} \quad (10)$$

and the theoretical relationship for the breakpoint (Fig. 7)

$$t_{cr} = \frac{m_i - m_{cr}}{V_1} \quad (11)$$

eqn. (6) can be rewritten:

$$m = m_s + \frac{m_{cr} - m_s}{\exp\left(-\frac{m_i - m_{cr}}{m_{cr} - m_s}\right)} \exp\left(-\frac{V_i}{m_{cr} - m_s} t\right) \quad (12)$$

This represents the theoretical drying curve (mass as a function of time) in terms of the four variables m_{cr} , m_i , m_s and V_i , which have to be estimated for each drying experiment by means of a fitting procedure. This optimisation has been accomplished by using the Hooke method. The computer program which finally delivers D according to eqn. (9) is given in the

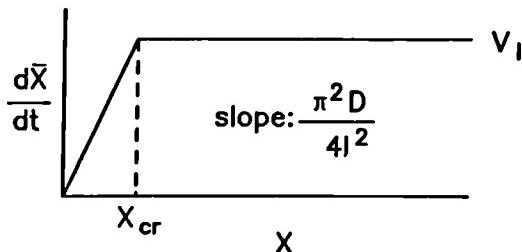


Fig. 7. Idealised drying curve, $m=f(\text{time})$.

Appendix. The apparent diffusion coefficients D_2 (the subscript 2 refers to method 2) and the corresponding critical moisture contents X_{cr} are listed in Table 2.

3. Determination of D by Graphical Method

The graphical method is based on a 'best eye fit' to determine the linear part of the drying curve (moisture content as a function of time) and thereby the critical moisture content and the constant drying rate in the initial drying period (Fig. 8). The apparent diffusion coefficients D_3 evaluated according to eqn. (9) are also listed in Table 3.

In most cases the participants repeated their measurements under near-constant experimental conditions, so that the results could be grouped and mean values and standard deviations for the apparent diffusion coefficients calculated. These results, together with the mean bed thickness and the number of drying runs included, are given in Table 2.

TABLE 2
MEAN VALUES OF DIFFUSION COEFFICIENTS DETERMINED BY DIFFERENT METHODS AND VARIOUS AUTHORS

Lab. ^a	<i>T</i> (mm)	<i>T</i> (°C)	ϕ (%)	u ($m s^{-1}$)	Exp. no.	$D/10^{-8} m^2 s^{-1}$								
						<i>n</i>	D_1	<i>s</i>	<i>n</i>	D_2	<i>s</i>	<i>n</i>	D_3	<i>s</i>
7	8·9	60	60	1·5	1-4	4	1·75	0·10	4	0·67	0·22	4	0·83	0·05
	3·1	60	40	2·0	5	—	—	—	1	0·52	—	1	1·04	—
	4·6	60	40	2·0	6-10	5	1·68	0·26	4	1·41	0·37	5	1·11	0·11
	6·4	60	40	2·0	11-15	5	2·12	0·29	5	1·50	0·73	5	1·74	0·26
	8·0	60	40	2·0	16-20	5	1·63	0·11	5	2·02	0·28	5	2·00	0·15
	16·3	60	40	2·0	21	1	4·13	—	1	2·90	—	1	3·53	—
16	7·9	60	6	1·3	22-26	5	6·31	0·54	5	2·90	0·37	5	4·17	0·93
	8·0	55	26	1·3	27-31	5	2·92	0·91	5	1·80	0·63	5	2·71	0·60
19	8·8	60	45	2·0	32-36	5	2·88	0·53	1	1·59	—	5	1·66	0·47
	7·2	60	45	2·0	37-40	4	3·05	0·55	4	1·02	0·46	4	1·74	0·21
	3·8	60	45	2·0	41-44	4	2·07	0·64	2	0·55	0·11	—	—	—
	5·3	60	45	2·0	45-48	4	3·36	1·75	1	0·78	—	4	1·58	0·21
	4·1	60	40	2·0	49-51	3	2·54	0·40	2	0·59	0·25	3	1·00	0·07
	5·8	60	40	2·0	52-54	3	3·12	0·68	2	0·71	0·11	3	1·19	0·14
	7·8	60	40	2·0	55-59	5	2·95	0·47	5	1·87	0·40	5	2·13	0·55
11	8·4	60	35	2·0	60-62	3	4·61	0·33	3	2·88	0·12	3	3·28	0·37
	8·6	60	58	2·0	63	1	4·38	—	1	4·90	—	1	4·58	—
	8·6	60	45	1·4	64-68	5	5·22	0·80	5	3·54	0·72	5	4·10	1·18
4	8·2	60	18	1·8	69	1	5·83	—	1	5·47	—	1	4·45	—
	4·3	60	18	1·8	70	1	2·47	—	1	3·46	—	1	3·86	—
17	9·0	60	60	2·0	71-77	7	1·83	0·31	7	2·06	0·31	7	2·00	0·61
	7·5	60	60	2·0	78-82	5	1·13	0·30	4	1·98	0·66	5	2·04	0·39
	5·4	60	60	2·0	83-86	2	0·56	0·35	—	—	—	4	2·67	0·75
	3·8	60	60	2·0	87-91	4	0·35	0·05	—	—	—	5	0·40	0·07

^aNumber refers to Table 2 in Chapter 2.

TABLE 3
EXTERNAL DRYING CONDITIONS AND DIFFUSION COEFFICIENTS DETERMINED BY DIFFERENT METHODS

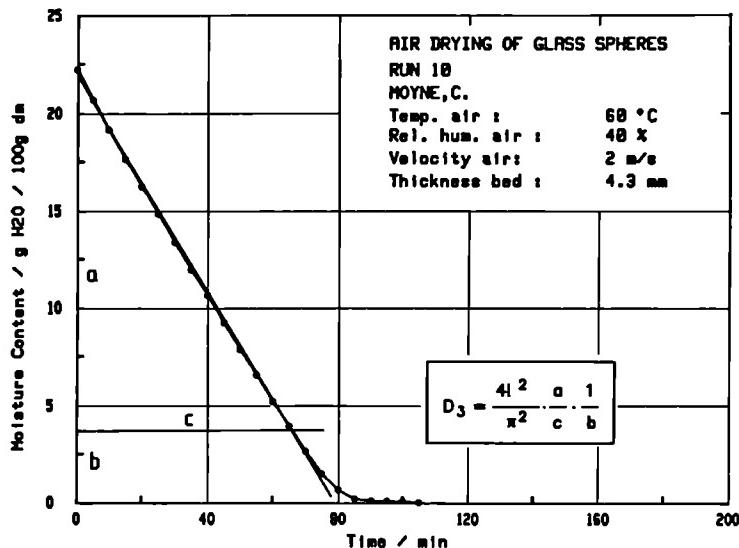
<i>Number</i>	<i>l</i> (mm)	ϕ (%)	<i>u</i> ($m s^{-1}$)	<i>T</i> (°C)	D_1 ($E - 8 m^2 s^{-1}$)	X_{cr} (%)	D_2 ($E - 8 m^2 s^{-1}$)	X_{cr} (%)	D_3 ($E - 8 m^2 s^{-1}$)	X_{cr} (%)
1	8.75	60	1.5	60	1.67	2.47	0.62	6.99	0.80	5.04
2	8.71	60	1.5	60	1.81	2.17	0.56	7.34	0.90	4.70
3	8.90	60	1.5	60	1.65	2.19	0.51	7.18	0.80	4.80
4	9.10	60	1.5	60	1.86	2.23	0.99	4.32	0.80	5.04
5	3.10	40	2.0	60	—	—	0.52	4.99	1.04	2.40
6	4.90	40	2.0	60	1.62	2.19	1.03	3.56	1.05	3.48
7	4.70	40	2.0	60	2.07	2.01	—	—	1.19	3.48
8	4.50	40	2.0	60	1.54	2.87	1.25	3.58	1.20	3.65
9	4.50	40	2.0	60	1.38	2.81	1.89	2.07	1.17	3.30
10	4.30	40	2.0	60	1.79	1.90	1.48	2.36	0.96	3.65
11	6.50	40	2.0	60	1.88	2.53	1.10	4.44	2.12	2.26
12	6.60	40	2.0	60	1.87	2.89	2.66	2.05	1.90	2.96
13	6.30	40	2.0	60	2.01	2.90	1.36	4.34	1.47	4.00
14	6.30	40	2.0	60	2.53	2.11	0.72	7.81	1.58	3.48
15	6.50	40	2.0	60	2.32	2.56	1.84	3.68	1.64	3.65
16	8.20	60	2.0	60	1.53	4.61	1.81	3.95	2.03	3.48
17	8.10	60	2.0	60	1.76	4.48	2.46	3.24	2.18	3.65
18	7.90	60	2.0	60	1.61	4.67	2.08	3.68	2.08	3.65
19	8.00	60	2.0	60	1.52	5.09	1.75	4.46	1.78	4.35
20	8.00	60	2.0	60	1.74	4.46	1.99	3.92	1.93	4.00
21	16.30	60	2.0	60	4.13	3.70	2.90	5.39	3.53	4.35
22	8.0	6	1.3	60	6.71	1.66	2.91	4.08	4.56	2.52
23	7.8	6	1.3	60	6.48	1.62	3.42	3.15	5.60	1.91
24	8.0	6	1.3	60	6.70	1.71	2.51	4.89	3.84	3.13
25	7.9	6	1.3	60	5.41	2.01	3.09	3.64	3.47	3.22
26	7.7	6	1.3	60	6.23	1.61	2.58	4.10	3.36	3.13
27	8.3	26	1.3	55	3.29	1.94	2.34	2.76	2.64	2.43
28	8.5	26	1.3	55	2.90	2.22	1.59	4.21	2.91	2.26

29	7.6	26	1.3	55	2.22	2.57	2.05	2.90	3.54	1.65
30	7.8	26	1.3	55	1.95	2.60	0.79	6.97	1.89	2.78
31	7.8	26	1.3	55	4.23	1.31	2.23	2.58	2.55	2.26
32	8.80	45	2.0	60	3.01	1.93	—	—	1.31	4.52
33	8.80	45	2.0	60	3.22	1.85	1.59	3.80	2.45	2.44
34	8.70	45	2.0	60	3.43	2.01	—	—	1.55	4.43
35	8.70	45	2.0	60	2.64	2.71	—	—	1.67	4.35
36	8.90	45	2.0	60	2.08	2.81	—	—	1.32	4.35
37	7.10	45	2.0	60	3.86	1.52	0.66	9.50	1.89	3.13
38	7.40	45	2.0	60	2.71	2.32	1.60	3.92	1.71	3.65
39	7.10	45	2.0	60	2.81	2.00	0.64	9.38	1.46	3.91
40	7.00	45	2.0	60	2.80	1.99	1.16	4.99	1.91	2.96
41	3.60	45	2.0	60	1.79	1.63	0.62	4.86	—	—
42	4.00	45	2.0	60	1.94	1.92	0.47	8.36	—	—
43	3.70	45	2.0	60	2.99	1.08	—	—	—	—
44	3.90	45	2.0	60	1.54	2.26	—	—	—	—
45	5.30	45	2.0	60	2.17	2.54	—	—	1.47	3.83
46	5.40	45	2.0	60	5.03	1.18	0.78	8.22	1.44	4.35
47	5.30	45	2.0	60	1.57	3.32	—	—	1.50	3.48
48	5.30	45	2.0	60	4.68	1.23	—	—	1.89	3.48
49	4.00	40	2.0	60	2.33	1.19	—	—	1.07	2.61
50	4.30	40	2.0	60	3.00	1.09	0.41	8.67	0.94	3.65
51	4.00	40	2.0	60	2.28	1.30	0.77	3.93	1.00	2.96
52	5.60	40	2.0	60	3.89	1.04	0.63	6.79	1.06	3.91
53	5.80	40	2.0	60	2.59	1.63	—	—	1.18	3.65
54	5.80	40	2.0	60	2.88	1.46	0.79	5.56	1.33	3.22
55	7.80	40	2.0	60	3.67	1.65	1.21	5.24	1.63	3.83
56	7.80	40	2.0	60	2.98	2.04	2.27	2.72	1.86	3.04
57	7.90	40	2.0	60	2.56	2.40	2.05	3.02	3.06	2.00
58	7.80	40	2.0	60	2.51	2.36	1.88	3.18	1.96	3.04
59	7.80	40	2.0	60	3.04	2.02	1.94	3.23	2.15	2.87
60	8.40	35	2.0	60	4.99	2.76	2.84	5.00	4.02	3.48
61	8.40	35	2.0	60	4.35	3.06	2.78	4.91	3.26	4.17
62	8.40	35	2.0	60	4.50	3.21	3.02	4.90	2.57	5.74

(continued)

• TABLE 3—conta

Number	<i>l</i> (mm)	ϕ (%)	<i>u</i> ($m s^{-1}$)	<i>T</i> (°C)	D_1 ($E - 8 m^2 s^{-1}$)	X_{cr} (%)	D_2 ($E - 8 m^2 s^{-1}$)	X_{cr} (%)	D_3 ($E - 8 m^2 s^{-1}$)	X_{cr} (%)
63	8.60	58	2.0	60	4.38	3.69	4.90	3.27	4.58	3.48
64	8.60	45	1.4	60	6.05	2.46	4.11	3.69	4.36	3.48
65	8.50	45	1.4	60	5.95	2.44	4.28	3.55	5.85	2.16
66	8.70	45	1.4	60	4.18	3.45	2.74	5.33	4.25	3.30
67	8.60	45	1.4	60	5.18	2.84	2.82	5.40	3.05	4.96
68	8.80	45	1.4	60	4.73	3.10	3.74	3.97	2.97	5.04
69	8.20	18	1.8	60	5.83	2.88	5.47	3.11	4.45	3.83
70	4.30	18	1.8	60	2.47	2.97	3.46	2.13	3.86	1.91
71	8.75	60	2.0	60	0.72	7.02	1.53	3.34	0.99	5.22
72	8.96	60	2.0	60	1.41	3.79	1.88	2.89	1.58	3.48
73	8.87	60	2.0	60	1.37	6.04	2.28	3.70	1.57	5.39
74	9.09	60	2.0	60	1.41	6.06	2.33	3.74	2.49	3.48
75	9.03	60	2.0	60	1.55	3.45	2.07	2.59	2.42	2.26
76	8.92	60	2.0	60	1.51	3.53	1.92	2.78	2.39	2.26
77	9.05	60	2.0	60	1.68	3.34	2.40	2.33	2.54	2.26
78	7.48	60	2.0	60	1.17	5.35	—	—	2.74	2.09
79	7.90	60	2.0	60	1.59	3.89	2.97	2.08	1.91	3.13
80	7.32	60	2.0	60	0.89	6.18	1.77	3.20	1.86	2.96
81	7.27	60	2.0	60	0.85	6.31	1.58	3.52	1.82	2.96
82	7.31	60	2.0	60	1.17	4.84	1.61	3.51	1.87	2.96
83	5.56	60	2.0	60	—	—	—	—	2.55	1.39
84	5.21	60	2.0	60	0.80	4.08	—	—	3.72	0.87
85	5.38	60	2.0	60	—	—	—	—	2.47	1.39
86	5.29	60	2.0	60	0.31	10.25	—	—	1.93	1.74
87	3.86	60	2.0	60	0.39	8.83	—	—	0.37	9.22
88	3.94	60	2.0	60	—	—	—	—	0.51	7.30
89	3.72	60	2.0	60	0.32	9.75	—	—	0.35	8.52
90	3.44	60	2.0	60	0.28	9.28	—	—	0.34	7.65
91	3.84	60	2.0	60	0.39	7.82	—	—	0.46	6.96

Fig. 8. Graphical determination of D .

DISCUSSION

Considering Table 3, it is remarkable that in a few cases the various calculation methods did not yield any result. Of special interest are those experiments where one calculation method yielded results whereas another did not. In most of these cases the data sets were not suitable for the calculation method used due to too long an initial drying period or even a non-existent second drying period. Therefore, for the interpretation and discussion of results only those experimental data sets were included for which it was possible to calculate apparent diffusion coefficients by all three methods.

Mean Apparent Diffusion Coefficients

From the remaining 65 data sets, mean values, standard deviations and confidence intervals for the apparent diffusion coefficients could be calculated for each of the three methods (Fig. 9).

Method 2 gave the smallest mean apparent diffusion coefficient (D_2) with the smallest standard deviation. The results of method 3 are comparable to

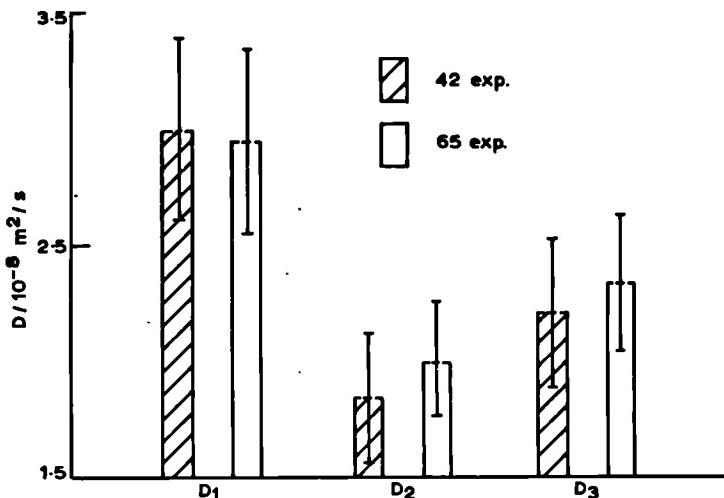


Fig. 9. Confidence interval ($P = 95\%$) of mean diffusion coefficients determined by various methods.

those of method 2, whereas methods 1 and 2 yielded significantly different results.

A further reduction of the data to 42 experimental sets is possible and advisable considering the wide spread of relative humidity values of the air from 6 to 60%. If only those experiments which had been carried out at 'moderate' relative humidities of 26–45% are included in the calculation of mean apparent diffusion coefficient, only slight quantitative changes occur, whereas the qualitative aspects remain nearly the same (Fig. 9). Applying the *F*-test to the variances of the three methods, no difference is found between methods 1 and 3 or between 2 and 3, whereas a difference between methods 1 and 2 seems to be probable.

By applying the *t*-test to the mean apparent diffusion coefficients determined by the three methods, no difference between methods 2 and 3 is detected, whereas the mean values determined by methods 1 and 3 are significantly different and those determined by methods 1 and 2 are highly significantly different.

Selection of Calculation Method

In view of the results obtained and the convenience of handling, it seems that the graphical method is the method of choice. One drawback, however,

is the fact that the method is not as objective as methods 1 and 2. Methods 1 and 2, on the other hand, are both very delicate so far as determination of the end of the drying experiment is concerned. Furthermore, for either method adequate computers are required. Since good agreement between the results of methods 2 and 3 was found, and due to the fact that the evaluation of the results calculated by method 1 was often difficult and also somewhat arbitrary (e.g. selection of degree of regression polynomial), method 2 can be recommended for use. However, the graphical method should be used in addition to confirm the results of method 2.

Irrespective of the methods used it is possible to improve the precision of the collaborative experiment by closer observance of the specified external drying conditions. The following limits should be observed:

temperature	$\pm 1^{\circ}\text{C}$
relative humidity	$\pm 2.5\%$
air velocity	$\pm 0.1 \text{ m s}^{-1}$
(bed thickness)	0.1 mm

Adequate attention should be paid to heat transfer. The dishes should be adequately insulated to ensure that heat transfer is effectively only via the surface of the glass sphere bed.

Influence of Bed Thickness on Diffusion Coefficient

If all individual experiments which yielded results with all of the three methods (65 experiments) are taken into account and grouped together to ascertain if a linear correlation between apparent diffusion coefficients and bed thickness exists, only for the apparent diffusion coefficients determined by the graphical method has a weak correlation been found to exist. If the influence of relative humidity which tends to oppose the influence of bed thickness is reduced in such a way that only those experiments carried out at relative humidities between 26 and 45% are included in the correlation analysis—and furthermore where bed thickness was between 4 and 8 mm—a weak correlation between the mean apparent diffusion coefficient determined by the three methods and the bed thickness could be detected. This result is also in agreement with the results of the correlation analyses within the individual laboratories, where in most cases weak positive correlations between the apparent diffusion coefficients and bed thickness and weak negative correlations between apparent diffusion coefficients and relative air humidity have been found.

CONCLUSION

Whatever the actual physical significance of the measured property, the work done by the group allows some conclusions to be drawn. In situations where true diffusion occurs, there are other problems to overcome such as variable diffusivity and the existence of a regular regime. Nevertheless, the problems approached during the study of the present case are fundamental.

The following conclusions can be drawn:

- Satisfactory experimental conditions for representative drying-rate measurements are always difficult to achieve. In that respect the drying of beds of glass microspheres is a very special case for a calibration exercise because of the short duration of the falling-rate period. Attention should be drawn to the need for the maximum number of experimental points and very precise control of temperature and humidity. Accordingly, automatic data generation is highly advisable.
- Modelling a drying curve with two linear sections can be useful for engineering purposes. To achieve this three methods were examined; analysis of the curve of mass versus time, represented by a linear and an exponential section, gave the best results.

The representativeness of an apparent diffusion coefficient extracted from drying curves depends on satisfying numerous physical assumptions, on experimental conditions, and on the method of calculation. Since the experimental conditions in the different laboratories taking part in the collaborative experiment varied widely, the scatter of results among laboratories is considerable. (The mean apparent diffusion coefficient has been found to be, for six laboratories and 42 experiments, $1.84 \times 10^{-8} \text{ m}^2 \text{s}^{-1}$ with a standard deviation of $0.94 \times 10^{-8} \text{ m}^2 \text{s}^{-1}$.)

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APPENDIX

```

10 ! NAME OF PROGRAM 'DIFFDRY'
20 ! GJ 10/85      VERSION 18.08.86
30 ! CALCULATION OF DIFFUSION COEFFICIENT ACC. TO TWO DIFFERENT METHODS
40 !METHOD 1: DRYING RATE CURVE
50 !METHOD 2: DRYING CURVE; m=mf(time)
60 !ORIGINAL PROGRAM WRITTEN BY MOYNE,C. (NANCY) IN FORTRAN 77,BASIC
70 !MODIFIED BY JUNG, G. (KARLSRUHE) IN HP-BASIC (AP2.0)
80 !
90 ! THE DATA-FILE (IN LINE 300) HAS TO BE WRITTEN IN THE FOLLOWING WAY:
100 ! A$      NAME OF AUTHOR
110 ! Nr     NUMBER OF EXPERIMENT
120 ! D$      DATE (DD.MM.YY)
130 ! Hoe    THICKNESS OF BED
140 ! Rf     RELATIVE HUMIDITY OF AIR
150 ! Lgsch   VELOCITY OF AIR (IN M/S)
160 ! Ttemp   TEMPERATURE OF AIR
170 ! Tgsch   DRYING RATE, ESTIMATED INITIAL VALUE (FLUX FIRST PERIOD
180 !           IN G/MIN)
190 ! Kg      CRITICAL MASS, ESTIMATED INITIAL VALUE
200 ! Eg      DRY MASS, ESTIMATED INITIAL VALUE
210 ! Ag      INITIAL MASS, ESTIMATED INITIAL VALUE
220 ! Npt    NUMBER OF MEASURING POINTS
230 ! Temps, Masse  MEASURING PROTOCOL (TIME,MASS)
240 !
250 DIM Temps(300),Masse(300),A(11,11),B(11),Ux(20),A$(25)
260 COM X(300),Y(300),Npt
270 !=====
280 !      READING OF EXPER. VALUES FROM DATAFILE
290 !=====
300 INPUT "NAME OF DATA FILE",A$
310 INPUT "CALCULATION ACCORDING TO METHOD 1 OR 2 ? (1,2)",S$
320 IF S$="2" THEN
330   CALL Tr3(A$)
340 ELSE
350   IF S$="1" THEN GOTO 380
360 END IF
370 GOTO 310
380 ASSIGN @in TO A$;"INTERNAL,4,1"
390 ENTER @in;A$,Nr,D$,Hoe,Rf,Lgsch,Ttemp,Tgsch,Kg,Eg,Ag,Npt
400 FOR I=1 TO Npt
410   ENTER @in;Temps(I),Masse(I)
420 NEXT I
430 Psec=Masse(Npt)
440 Temps(1)=1.E-10
450 !PRINTER IS 701
460 PRINT "NUMBER OF EXPER.: ";Nr
470 PRINT
480 PRINT
490 PRINT "NUMBER OF POINTS: ";Npt
500 PRINT
510 PRINT
520 FOR I=1 TO Npt
530   PRINT Temps(I),Masse(I)
540 NEXT I
550 PRINT CHR$(12)
560 PRINTER IS 1
570 ASSIGN @Out4 TO "FILE_13"
580 !=====
590 !      IN FILE_13 : DRYINGCURVE
600 !=====
610 !
620 !
630 !=====
640 !      CALCULATION
650 !=====
660 !
670 INPUT "DEGREE OF POLYNOM",N
680 INPUT "NUMBER (ODD) OF POINTS PER STEP?",M
690 R=(M-1)/2
700 Nptv=Npt+1-M

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710 IF INT(M/2)=M/2 OR M<N+1 THEN
720   BEEP 500,1
730   PRINT "BAD SELECTION OF FITTING PARAMETER"
740   GOTO 670
750 END IF
760 OUTPUT @Out4;Nptv
770 FOR I=1 TO (M-1)/2
780   Ux(I)=(Mass(I)/Psec-1)*100
790 NEXT I
800 PRINT "*****"
810 PRINT "*"
811 PRINT "          ";A$;"           ";"NR. OF EXP. : ";Nr
830 PRINT
840 PRINT "           CALCULATION ACC. TO METHOD 1"
850 PRINT "*****"
860 PRINT
870 PRINT
880 PRINT
890 PRINT "DEGREE OF POLYNOM= ";N$, " NUMBER OF POINTS= ";M$, " DRYMASS= ";Psec
900 PRINT
910 PRINT
920 PRINT "TIME      MASS      MOISTURE      MASS,C. MOISTURE,C. VS      VS,C."
930 FOR I=1 TO (M-1)/2
940   PRINT PROUND(Temp(I),-3), PROUND(Mass(I),-3), PROUND(Ux(I),-3)
950 NEXT I
960 FOR K=1 TO Npt-M+1
970   FOR I=1 TO N+1
980     FOR J=1 TO I
990       A(I,J)=0.
1000      FOR L=K TO K+M-1
1010        A(I,J)=A(I,J)+Temp(L)^((I+J-2))
1020      NEXT L
1030      A(J,I)=A(I,J)
1040    NEXT J
1050    B(I)=0.
1060    FOR L=K TO K+M-1
1070      B(I)=B(I)+Mass(L)*Temp(L)^(I-1)
1080    NEXT L
1090  NEXT I
1100 CALL Gauss(A(*),B(*),N+1)
1110 Pmod=B(1)
1120 Vs=0.
1130 Tps=Temp(K+(M-1)/2)
1140 FOR L=2 TO N+1
1150   Pmod=Pmod+B(L)*Tps^(L-1)
1160   Vs=Vs-(L-1)*B(L)*Tps^(L-2)
1170 NEXT L
1180 U=(Mass(K+(M-1)/2)/Psec-1.)*100
1190 Umod=(Pmod/Psec-1.)*100
1200 Vsmod=Vs/Psec*6000
1210 PRINT PROUND(Temp(K+(M-1)/2),-3), PROUND(Mass(K+(M-1)/2),-3), PROUND(U,-3),
1220 PROUND(Pmod,-3), PROUND(Umod,-3), PROUND(Vs,-3), PROUND(Vsmod,-3)
1230 OUTPUT @Out4;Umod, Vsmod
1230 NEXT K
1240 FOR I=1 TO (M-1)/2
1250   Ux(I)=(Mass(Npt-(M-1)/2+I)/Psec-1.)*100
1260 NEXT I
1270 FOR I=Npt-(M-3)/2 TO Npt
1280   PRINT PROUND(Temp(I),-3), PROUND(Mass(I),-3), PROUND(Ux(I-Npt+(M-1)/2),-3)
1290 NEXT I
1300 PRINT
1310 PRINT
1320 PRINT
1330 ASSIGN @Out4 TO *
1340 INPUT "WOULD YOU LIKE ANOTHER DEGREE OF POLYNOM? (Y/N)",S$
1350 IF S$="Y" THEN GOTO 570
1360 IF S$="N" THEN GOTO 1380
1370 GOTO 1340
1380 PRINT CHR$(12)

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1390 CALL Tr2s(Hoe)
1400 END
1410 !=====
1420 ! ===== SUBPROGRAM 'GAUSS' =====
1430 !
1440 SUB Gauss(A(*),B(*),M)
1450   FOR I=1 TO M
1460     A(I,M+1)=B(I)
1470   NEXT I
1480   FOR Kk=1 TO M-1
1490     Pivot=A(Kk,Kk)
1500     FOR K1=Kk TO M
1510       IF ABS(Pivot)>ABS(A(K1,Kk)) THEN 1540
1520       Line=K1
1530       Pivot=A(K1,Kk)
1540     NEXT K1
1550     IF ABS(Pivot)<1.E-5 THEN 1810
1560     IF Line=Kk THEN 1620
1570     FOR I=Kk TO M+1
1580       Pivot=A(Kk,I)
1590       A(Kk,I)=A(Line,I)
1600       A(Line,I)=Pivot
1610     NEXT I
1620     FOR I=Kk+1 TO M
1630       IF ABS(A(I,Kk))<1.E-5 THEN 1690
1640       F=A(I,Kk)/A(Kk,Kk)
1650       FOR Jj=Kk+1 TO M+1
1660         IF ABS(A(Kk,Jj))<1.E-5 THEN 1680
1670         A(I,Jj)=A(I,Jj)-F*A(Kk,Jj)
1680       NEXT Jj
1690     NEXT I
1700   NEXT Kk
1710   IF ABS(A(M,M))<1.E-5 THEN 1810
1720   B(M)=A(M,M+1)/A(M,M)
1730   FOR I=M-1 TO 1 STEP -1
1740     FOR Kk=I+1 TO M
1750       IF ABS(A(I,Kk))<1.E-5 THEN 1770
1760       Sum=Sum+A(I,Kk)*B(Kk)
1770     NEXT Kk
1780     B(I)=(A(I,M+1)-Sum)/A(I,I)
1790   NEXT I
1800   GOTO 1820
1810   PRINT "SINGULAR MATRIX"
1820 SUBEND
1830 !***** SUBPROGRAM TO READ DATA FROM FILE 13 FOR CALCULATING
1840 ! DRYING RATE CURVE
1850 !***** "SUB Uvwerte(U(*),V(*),Nn)
1860 !***** MASS STORAGE IS ":INTERNAL,4,0"
1870 "SUB Uvwerte(U(*),V(*),Nn)
1880   MASS STORAGE IS ":INTERNAL,4,0"
1890   OPTION BASE 1
1900   DIM A(300),B(300)
1910   ASSIGN @In TO "FILE_13"
1920   ON ERROR GOTO 1950
1930   ENTER @In;Nn
1940   ENTER @In;A(*)
1950   OFF ERROR
1960   L=1
1970   FOR I=1 TO Nn*2 STEP 2
1980     U(L)=A(I)
1990     V(L)=A(I+1)
2000     L=L+1
2010   NEXT I
2020 SUBEND
2030 !***** SUBPROGRAM TR2
2040 "SUB Tr2s(Hoe)
2050 !***** "SUB Tr2s(Hoe)
2060   DIM U(300),V(300)
2080   CALL Uvwerte(U(*),V(*),Nn)
2090   Npt=Nn
2100   Smi=1000
2110   N=0

```

```

2120 FOR I=2 TO Npt
2130   Ucr=U(I)
2140   A=0
2150   B=0
2160   FOR J=1 TO Npt
2170     X1=
2180     IF (U(J)<Ucr) THEN X=U(J)/Ucr
2190     A=A+V(J)*X
2200     B=B+X^2
2210   NEXT J
2220   V1=A/B
2230   S=0
2240   FOR J=1 TO Npt
2250     X1=
2260     IF (U(J)<Ucr) THEN X=U(J)/Ucr
2270     S=S+(V(J)-X*V1)^2
2280   NEXT J
2290   PRINT "UCr=";Ucr,"V1=";V1,"S=";S
2300   IF S<Smn THEN
2310     Smn=S
2320   Uc=Ucr
2330   Vp=Vm
2340   Vm=V1
2350   Icr=I
2360   ELSE
2370     N=N+1
2380   END IF
2390   IF N>3 THEN 2410
2400   NEXT I
2410   A=0
2420   B=0
2430   FOR I=Icr TO Npt
2440     A=A+U(I)^2
2450     B=B+U(I)*V(I)
2460   NEXT I
2470   C=0
2480   FOR I=1 TO Icr-1
2490     C=C+V(I)
2500   NEXT I
2510   Uc1=A*C/B/(Icr-1)
2520   Vc1=Uc1*B/A
2530   A=A-U(Icr)^2
2540   B=B-U(Icr)*V(Icr)
2550   C=C+V(Icr)
2560   Uc2=A*C/B/Icr
2570   Vc2=Uc2*B/A
2580   S1=0
2590   S2=0
2600   FOR I=1 TO Npt
2610     X1=1
2620     X2=1
2630     IF I>Icr-1 THEN X1=U(I)/Uc1
2640     IF I>Icr THEN X2=U(I)/Uc2
2650     S1=S1+(V(I)-Vc1*X1)^2
2660     S2=S2+(V(I)-Vc2*X2)^2
2670   NEXT I
2680   PRINT
2690   PRINT
2700   PRINT "U(ICR+1)=";U(Icr+1),"UC2=";Uc2,"U(ICR)=";U(Icr),"VC2=";Vc2,"S2=";
2710   S2
2720   PRINT
2730   PRINT "U(ICR)=";U(Icr),"UC1=";Uc1,"U(ICR-1)=";U(Icr-1),"VC1=";Vc1,"S1=";
2740   S1
2750   Uc=Uc1
2760   Vc=Vc1
2770   S=S1
2780   Vmoy=0
2790   S2=0
2800   H=Hoe
2790   D=1.1258E-10*H^2*Vc/Uc
2800   FOR I=1 TO Npt
2810     Vmoy=Vmoy+V(I)
2820     S2=S2+V(I)^2

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2830 NEXT I
2840 Vmoy=Vmoy/Npt
2850 R=SQRT(1-S/(S2-Npt*Vmoy^2))
2860 PRINT
2870 PRINT
2880 PRINT
2890 PRINT "CRITICAL MOISTURE=";Uc,"DRYING RATE FIRST PHASE=";Vc
2900 PRINT "DIFFUSION COEFFICIENT IN M^2/S:";D
2910 PRINT "COEFFICIENT OF REGRESSION=";R
2920 PRINT
2930 PRINT
2940 SUBEND
2950 !*****SUBPROGRAM TR3
2960 ! ATTENTION: LONG CPU TIME (15 MIN.) POSSIBLE!!
2970 !*****SUBPROGRAM TR3
2980 !*****SUBPROGRAM TR3(Aa)
2990 SUB Tr3(Aa)
3000 COM X(300),Y(300),Npt
3010 DIM Z(15),H(15),Title$[80],Fichier#[10],N#[30],A#[25]
3020 ASSIGN @In TO Aa$#"INTERNAL,4,1"
3030 ENTER @In;A$,Nr,D$,Hoe,Rf,Lgsch,Ttemp,Tgsch,Kg,Eg,Ag,Npt
3040 Th=Hoe
3050 FOR I=1 TO Npt
3060   ENTER @In;X(I),Y(I)
3070 NEXT I
3080 ASSIGN @In TO *
3090 PRINTER IS 1
3100 N=4
3110 Z(1)=Tgsch
3120 Z(2)=Kg
3130 Z(3)=Eg
3140 Z(4)=Ag
3150 H(1)=.001
3160 H(2)=.1
3170 H(3)=.1
3180 H(4)=.1
3190 Eps=-1
3200 PRINT "INITIAL VALUES AND STEPS"
3210 PRINT
3220 FOR I=1 TO N
3230   PRINT Z(I),H(I)
3240 NEXT I
3250 CALL Hooke(Estim,Fcoud,Z(*),H(*),N,Eps,Komp)
3260 E$=VAL$(E1)
3270 PRINT "*****"
3280 PRINT
3290 PRINT "          NAME ";A$;"           NR. OF EXPERIMENT";Nr
3300 PRINT
3310 PRINT "          CALCULATION ACC. TO METHOD 2"
3320 PRINT
3330 PRINT "*****"
3340 PRINT
3350 PRINT
3360 FOR I=1 TO Npt
3370   Yc=FNEstim(X(I),Z(*))
3380   E=Y(I)-Yc
3390   PRINT X(I),Y(I),Yc,E
3400 NEXT I
3410 Y1=(Z(4)/Z(3)-1)*100
3420 Ycr=(Z(2)/Z(3)-1)*100
3430 V1=Z(1)*6000/Z(3)
3440 D=4.0528E-7#Z(1)/(Z(2)-Z(3))*Th*Th/60
3450 PRINT
3460 PRINT
3470 PRINT "DRY MASS      = ";Z(3);"g    HEIGHT    = ";Th;" mm"
3480 PRINT "INITIAL MASS  = ";Z(4);"g    YI      = ";Yi;" %"
3490 PRINT "CRITICAL MASS = ";Z(2);"g    YCr     = ";Ycr;" %"
3500 PRINT "FLUX FIRST PERIOD   = ";Z(1);" g/min"
3510 PRINT "VELOCITY FIRST PERIOD = ";Vi;" %/h"
3520 PRINT "DIFFUSION COEFFICIENT = ";D;" m^2/s"
3530 PRINT

```

```

3540 STOP
3550 SUBEND
3560 !***** DEF. FUNCTION FCOUT *****
3570 ! DEF. FUNCTION FCOUT
3580 !***** DEF. FUNCTION FCOUT *****
3590 DEF FNFCout(Z(*),Estim)
3600   COM X(300),Y(300),Npt
3610   Fcoud=0
3620   FOR I=1 TO Npt
3630     Fcoud=Fcoud+(Y(I)-FNEstim(X(I),Z(*)))^2
3640   NEXT I
3650   RETURN Fcoud
3660 FNEND
3670 !***** SUBPROGRAM Hooke *****
3680 ! SUBPROGRAM Hooke
3690 !***** SUBPROGRAM Hooke *****
3700 SUB Hooke(Estim,Fcoud,Z(*),H(*),N,Eps,Komp)
3710   DIM Zmo(15),Zm(15),Zh(15)
3720   Fmin=1.E+30
3730   Komp=0
3740   FOR I=1 TO N
3750     Zm(I)=Z(I)
3760     Zmo(I)=Z(I)
3770   NEXT I
3780   K=0
3790   FOR I=1 TO N
3800     Fz=FNFCout(Z(*),Estim)
3810     Zm(I)=Z(I)+H(I)
3820     Ifi=FNFCout(Zm(*),Estim)-Fz
3830     IF Ifi<0 THEN 3860
3840     IF Ifi=0 THEN 3940
3850     IF Ifi>0 THEN 3880
3860     K=1
3870     GOTO 3930
3880     Zm(I)=Z(I)-H(I)
3890     Ifj=FNFCout(Zm(*),Estim)-Fz
3900     IF Ifj<0 THEN 3920
3910     IF Ifj>0 THEN 3940
3920     K=1
3930     GOTO 3950
3940     Zm(I)=Z(I)
3950   NEXT I
3960   IF K<=0 THEN 3980
3970   IF K>0 THEN 4140
3980   Apz=(ABS(Fz-Fmin)/(ABS(Fz)+ABS(Fmin))-Eps)
3990   IF Apz<=0 THEN 4010
4000   IF Apz>0 THEN 4020
4010   GOTO 4310
4020   Komp=Komp+1
4030   PRINTER IS 1
4040   PRINT Komp
4050   FOR I=1 TO N
4060     PRINT Z(I),H(I)
4070   NEXT I
4080   Fmin=Fz
4090   IF Komp-7<=0 THEN 4110
4100   IF Komp-7>0 THEN 4010
4110   FOR I=1 TO N
4120     H(I)=H(I)/2
4130   NEXT I
4140   FOR I=1 TO N
4150     Zh(I)=2*Zm(I)-Zmo(I)
4160   NEXT I
4170   Ifk=FNFCout(Zh(*),Estim)-FNFCout(Zm(*),Estim)
4180   IF Ifk<0 THEN 4200
4190   IF Ifk>0 THEN 4260
4200   FOR I=1 TO N
4210     Z(I)=Zh(I)
4220     Zmo(I)=Zm(I)
4230     Zm(I)=Z(I)
4240   NEXT I
4250   GOTO 3780
4260   FOR I=1 TO N

```

```

4270      Z(I)=Zm(I)
4280      Zmo(I)=Zm(I)
4290      NEXT I
4300      GOTO 3780
4310      SUBEND
4320 !*****DEF. FUNCTION ESTIM*****
4330 !
4340 !*****DEF FNEstim(X,Z(*))
4350 DEF FNEstim(X,Z(*))
4360   T0=(Z(4)-Z(2))/Z(1)
4370   IF (X-T0)<=0 THEN 4390
4380   IF (X-T0)>0 THEN 4410
4390   Estim=Z(1)*X+Z(4)
4400   GOTO 4420
4410   Estim=Z(3)+EXP(-Z(1)*X/(Z(2)-Z(3)))*(Z(2)-Z(3))/EXP(-(Z(4)-Z(2))/(Z(2)-Z
(3)))
4420   RETURN Estim
4430 FNEND

```

DISCUSSION

K. P. Poulsen referred to recently-published results on a similar system by Japanese workers (Suzuki, 1980) who used a steady-state method in which the bed of glass beads was kept fed with water from a microsyringe at one end of the bed, evaporation into hot air taking place from a zone at the other end. They found great differences in diffusivity at different bed water contents ranging from 10^{-5} at 225 kg water m⁻³ bed volume to 10^{-8} at near-zero water content. COST 90bis results fit nicely into their range of results. *C. Moyne* replied that, as he had indicated, the system was not one of simple vapour diffusion but one in which liquid flow predominated at high moisture contents giving large effective diffusivities, falling to a minimum at lower moisture contents when vapour diffusion predominated and finally to possibly greater diffusivities at very low moisture contents. He stressed that the collaborative work was based on a very simple experiment to compare the results of workers in different parts of Europe and was not directed at detailed analysis of the chosen system. Poulsen added that the COST 90bis results lay on a part of the diffusivity/moisture content curve which according to Suzuki was linear.

E. W. Schlünder and *H. Schubert* raised questions regarding the details of the experiment and the degree of standardisation between the participants, asking that as well as diffusivities original drying-rate curves be included in the published Proceedings. (*Editor's note:* Because of the large number, this was not practicable. However, all original results were available to Wolf and Moyne for the analyses of the findings, and their paper includes as much original and derived information as space would allow. Readers interested in further details should contact the authors.)

M. Okos and his co-workers had also found diffusivity to vary by several orders of magnitude over the range of moisture contents in their drying experiments and questioned the wisdom of quoting a single value for diffusivity for the whole experiment. *Moyne* emphasised that the essence of the investigation was simplicity in order to determine whether a single value for diffusivity could, in simple engineering terms, describe the behaviour of this system. He agreed with *Okos* that in more complex systems such as foods any values for diffusivity must be related to the moisture content of the material. *Okos* also referred to the fact that in drying most foods there was no constant-rate period, so how could this kind of analysis be used for such purposes? *Moyne* agreed that the method might not be suitable and would always have to be used with caution.

R. Jowitt (the Project Leader) pointed out that the purpose of the exercise was *only* for the 'calibration' of the participants, not for its own sake. Much thought had gone into devising an experiment which would test the extent to which some 20 different participants would agree in their results of determining water diffusivity from a drying experiment on the *same* model system, using the *same* conditions and, as nearly as possible, the *same* kind of equipment. The conditions were progressively refined to ensure comparability and the outcome was, as can be seen from the paper under discussion, not perfect agreement, but reasonable agreement. It was never intended to simulate the drying of a foodstuff, only the *process* of such an operation. *E. Rotstein* welcomed the clarification by the Project Leader which put the work into the proper perspective but nevertheless emphasised how different circumstances were when dealing with diffusion and drying in living food materials which do not just provide a 'sorption field' but many other, much more complicated interactions. In the bed of glass microspheres, mass transfer was wisely and deliberately chosen to be controlling but in many food systems both heat and mass transfer were involved—and possibly also gravitation. It was necessary in most cases to include a convection component in the mass transfer term. Omission of this could well account for apparent discrepancies between values of diffusivity for ostensibly similar situations. With this, however, he wished to congratulate the participants on their valuable work.

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4

Diffusion in Shrinking Media: The Case of Drying of Gels

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SUMMARY

In order to extract diffusion coefficients from drying curves on shrinking products, progress has to be made in both experimental technique and data treatment. The practice of continuous measurement of gelatin-drying kinetics is analysed and discussed. Differential equations for heat and mass transport in non-porous shrinking colloidal materials are derived and solved numerically. A certain concentration dependence of the diffusion coefficient is assumed and the drying curve is simulated. Finally, comparison with experimental results should be a means of identification of the mass transport coefficient.

NOMENCLATURE

- D diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
 T temperature ($^\circ\text{C}$)
 V air velocity (m s^{-1})
 X moisture content
 e thickness of the coated film (m)
 m weight of sample (g)
 t time (s)
 v_i velocity of component i (m s^{-1})
 \bar{v}_i partial specific volume ($\text{m}^3 \text{kg}^{-1}$)
 ω_i mass fraction of component i

- z distance coordinate (m)
 ε \bar{v}_1/\bar{v}_2
 ξ reduced distance coordinate (m)
 ρ density (kg m^{-3})
 ϕ relative humidity

Subscripts

- 0 at time $t=0$
 1 component: water
 2 reference component: dry gelatin

Superscripts

- average value

1. INTRODUCTION

Food materials are often non-porous deformable substances, of which gelatine and similar gels are good models.

One of the purposes of COST 90bis is the determination of coefficients of diffusion in food products. Amongst several methods which have been proposed, the analysis of sorption and desorption experiments and of drying curves in the falling-rate regime are the most widely used.

This chapter will summarise some recommendations to facilitate proper use of the second method. Actually the shrinking nature of the product and the marked concentration dependence of the diffusion coefficients are the two major difficulties of the method. These difficulties will be analysed in three steps: (i) conditions for producing experimental results from gelatine slab drying; (ii) analytical and numerical methods for the simulation of drying curves with an assumed dependence by the diffusion coefficient on water content; and (iii) scope for further work on evaluation of the diffusion coefficient.

2. SAMPLE

Gels belong to the group of colloids which, in turn, is divided into three classes: (i) dispersoid, (ii) micelle, and (iii) polymers (synthetic and natural). The swelling polymers are gel-building substances. They include (i) physical gels where the cross-linking between macromolecules is of a physical nature and which show almost unlimited swelling such as gelatin and agar-agar,

and (ii) chemical gels like polyacrylamide with limited swelling. The interest in using gelatine, as in this study, lies in the fact that one-dimensional shrinking can be obtained. Owing to the physical nature of the bonding between molecules, a gelatine slab firmly attached to a flat 'perspex' plate shows an almost perfect shrinkage normal to the plate.

If ideal behaviour is assumed, the following relationship holds for shrinking gelatine:

$$e = e_2(1 + \varepsilon\bar{X}) \quad (\text{Ref. 1})$$

where e is the thickness of the film of average moisture content \bar{X} and e_2 is the bone-dry thickness (dried at 100°C for 24 h under vacuum).

3. EXPERIMENTAL PROCEDURE

In order to obtain accurate reproducible measurements, certain precautions are necessary. Air at constant temperature and humidity is passed through an equalising section containing grids and then fed to a horizontal duct (section 70 × 100 mm). The gel, on its plate, lies at the other end, level with the bottom of the duct. To ensure that there is no heat flux through the supporting slab 30-mm thick insulation is used (Fig. 1). The electronic scale

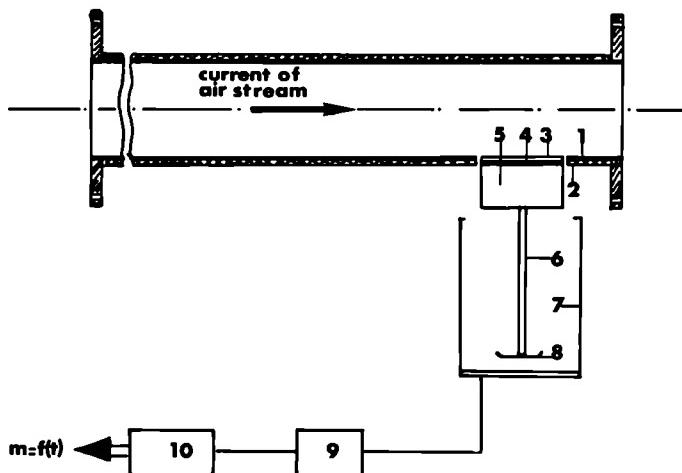
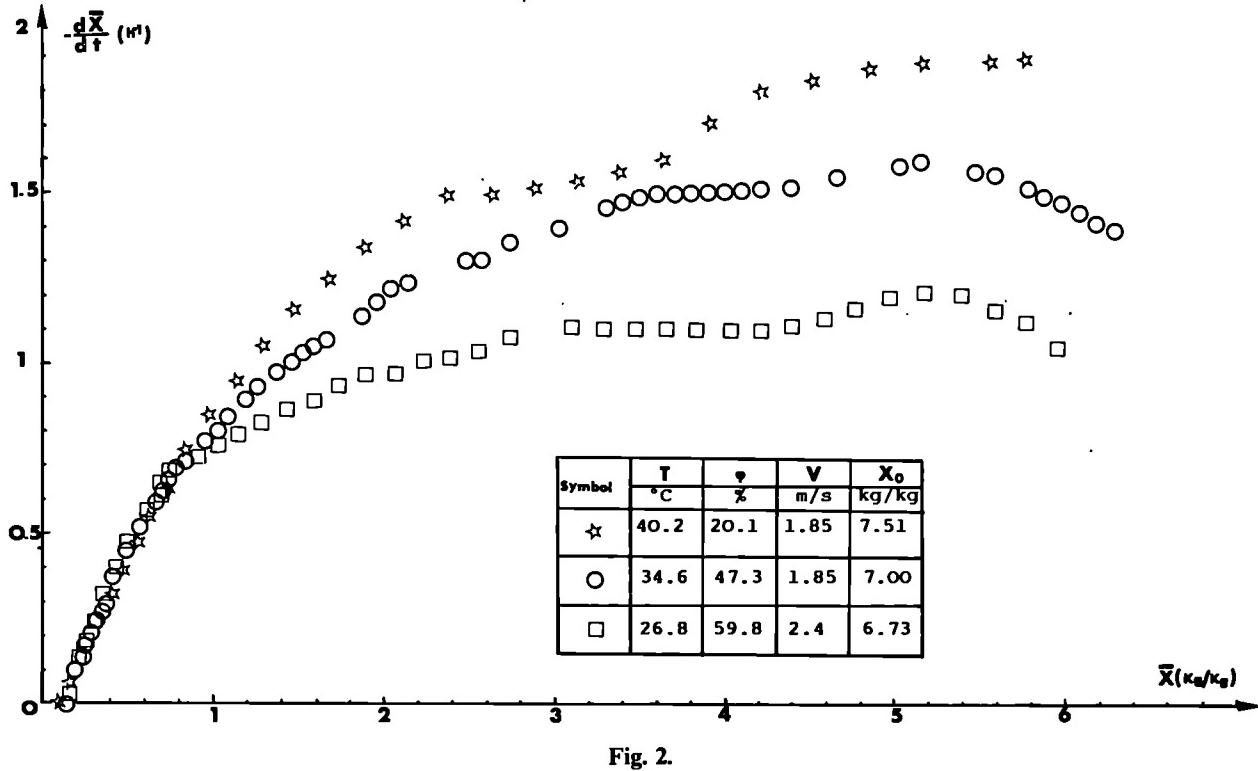


Fig. 1. 1, Floor of duct; 2, insulation; 3, gelatin gel; 4, 'perspex' plate; 5, expanded polystyrene; 6, support; 7, weighing chamber; 8, weighing pan; 9, analog-digital converter; 10, recording system.



itself delivers both analogue and digital signals. Data can be stored and processed by microcomputer.

4. EXAMPLES OF DRYING KINETICS

As first experiments, the drying of gelatin films was carried out at low temperatures (30–40°C) and medium relative humidity (20–60%). The average moisture content \bar{X} is recorded and plotted as a function of time. After differentiating with respect to time, the drying curve, showing the drying rate ($-d\bar{X}/dt$) versus the average moisture content, is produced according to the method described in Chapter 3.

Figure 2 shows some typical results: the constant drying-rate period can be affected by the attainment of uniform temperature by the body and by slight variations in relative humidity (see upper curve). Nevertheless, two periods in the falling-rate regime can be observed; the last one can be described as a regular regime common to all the different temperatures and relative humidities in the various ranges explored.

5. MATHEMATICAL MODELLING AND IDENTIFICATION

In shrinking systems it is necessary, in order to derive a model, to define fluxes in a component-centred coordinate reference system.^{2–4} A frame of reference must be found so that there is no net transfer of the reference component through a plane perpendicular to the flux.

For one-dimensional transfer the diffusion and the continuity equations for water are

$$\rho_1 v_1 = -\rho D \frac{\partial \omega_1}{\partial z} + \omega_1 (\rho_1 v_1 + \rho_2 v_2) \quad (1)$$

$$\frac{\partial \rho_1}{\partial t} = -\frac{\partial}{\partial z}(\rho_1 v_1) \quad (2)$$

Combining eqns. (1) and (2), after some rearrangement,

$$\frac{\partial \rho_1}{\partial t} = -\frac{\partial}{\partial z}(\rho_1 v_2) + \frac{\partial}{\partial z}\left(\frac{\rho D \partial \omega_1 / \partial z}{1 - \omega_1}\right) \quad (3)$$

The new coordinate ξ is defined by

$$\xi = \int_0^z \bar{v}_2 \rho_2 dz \quad (4)$$

So eqn. (3) becomes, in terms of water mass fraction X_1 ,

$$\frac{\partial X_1}{\partial t} = \frac{\partial}{\partial \xi} \left[\frac{D}{(1 + \varepsilon X_1)^2} \frac{\partial X_1}{\partial \xi} \right] \quad (5)$$

The material boundary conditions correspond to no mass transfer from the lower face of the gel and convective mass transfer from the upper face. The air humidity at the surface is given by the wet-bulb temperature conditions during the constant-rate period and by the hygroscopic equilibrium during the falling-rate regime.

The temperature is assumed uniform in the gel (thickness 4–0.2 mm). In the falling-rate regime a macroscopic heat balance gives this temperature. At this point it is proposed that a future task for the COST 90bis subgroup would be to solve numerically eqn. (5) with an assumed dependence of D on the local moisture content X_1 and, conversely, to try to identify the factors included in the D function by comparison with the experimental curves.

In order to achieve this goal, a complete set of drying curves for various conditions and for high initial moisture content is required.

6. CONCLUSIONS

This chapter presents some preliminary results of the 'Diffusion' subgroup of COST 90bis and proposes a plan for future action with respect to the drying of dimensionally unstable food-like materials. In order to obtain representative experimental results, particular attention should be directed towards automatic data acquisition and processing, and also to close control of the hydrodynamic, thermal and material boundary conditions around the sample.

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4. Gehrmann, D. (1979). Dr. Ing. Dissertation, Technische Hochschule, Darmstadt.

5

A Study of Moisture Transport in Minced Beef Products

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NOMENCLATURE

- X moisture content (g g^{-1} D.M.)
 X_e equilibrium moisture content (g g^{-1} D.M.)
 X_0 initial moisture content (g g^{-1} D.M.)

INTRODUCTION

Sherwood's model¹ has been used to determine the apparent diffusion coefficient of moisture in minced beef products.

EXPERIMENTAL CONDITIONS

Material

Slabs of raw minced lean beef
Heat-treated minced lean beef (85°C/15 min)

Principal Components

Fat	1·6%
Protein	20·5%
Water content	75·2%
pH	5·6

Drying Conditions

Drying took place from both sides of the slab
Air temperature constant within the range 30–75°C

Air velocity	2 m s^{-1}
Relative humidity	30%
Slab dimensions	thickness 3–4 mm length × width 60 × 60 mm
Initial moisture content	raw: 2.80 g g^{-1} D.M. heat-treated: 1.80 g g^{-1} D.M.
Initial solid temperature	on each occasion equilibrated in a sealed bag to corresponding wet-bulb temperature of air before exposure to drying conditions

RESULTS

During drying the meat slab shrinks considerably. At the end of the drying period the thickness has decreased by 30–40%. Changes in the thickness as a function of the moisture content were studied. The apparent diffusion coefficient is here calculated on the basis of the actual thickness of the slab, not of the initial thickness.

Figure 1 shows the change in thickness as a function of moisture content for (a) raw and (b) heat-treated minced lean beef at 40°C. For heat-treated minced beef the thickness decreases linearly with moisture content, whereas for raw minced beef the thickness decreases linearly with moisture content only to a certain level, after which it remains constant.

Figure 2 shows the change in $\ln(X - X_e)/(X_0 - X_e)$ with time. For raw

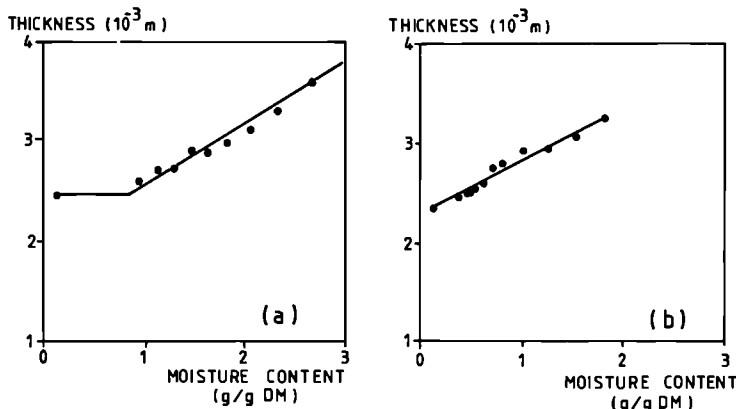


Fig. 1.

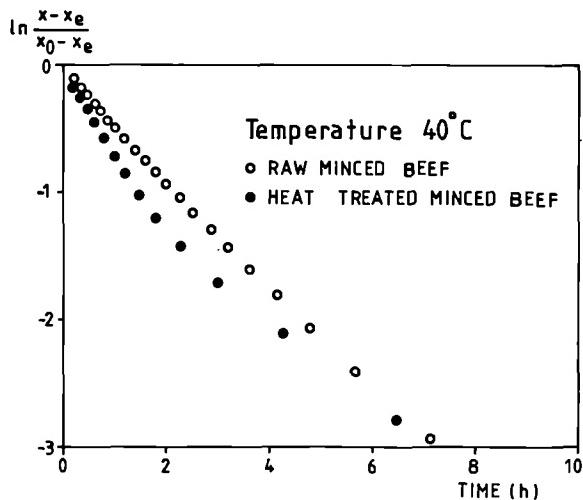


Fig. 2.

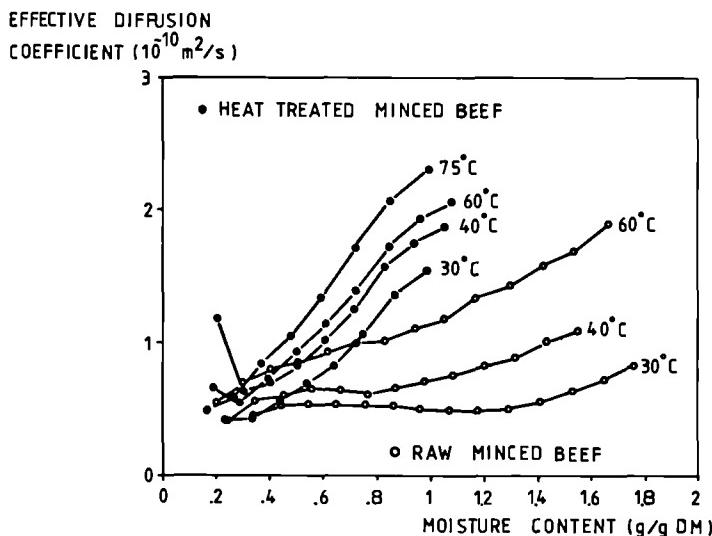


Fig. 3.

minced beef a nearly straight line is obtained, whereas for heat-treated minced beef the slope of the line changes. Because of the changes in the thickness of the slab during drying, this method leads to a variable apparent diffusion coefficient in both cases. This is illustrated in Fig. 3.

CONECLUSIONS

The apparent diffusion coefficient for water in raw and heat-treated minced beef changes with the moisture content.

For a given moisture content and temperature, the diffusion coefficient can be 2–3 times greater in heat-treated than in raw minced beef.

The apparent diffusion coefficient changes with temperature. According to the Arrhenius relationship, for heat-treated minced beef the energy of activation is about 13 kJ mole^{-1} . For raw minced beef depending on its moisture content it varies from about 8 to about 25 kJ mole^{-1} .

During these experiments the measurement of the thickness has been a critical concern in the determination of the apparent diffusion coefficient. As the sample does not shrink uniformly, it occasionally presents a very irregular surface. This made the measurement of the thickness very difficult. A variation of 30% in the thickness of the slab can sometimes be observed.

REFERENCE

1. Sherwood, T. K. (1932). The drying of solids—IV, *Ind. Eng. Chem.*, **24**(3), 307–10.

6

Diffusion Phenomena in Potato Drying

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Drying of potato slices was undertaken as a part of the COST 90bis programme. The aim was to establish relationships between drying temperature, relative humidity of the air, thickness of slices and drying time.

Young potatoes, variety Bintje with an initial dry matter of 16%, were bought in a local shop. Average diameter of potatoes was about 50 mm; 4·5, 7 and 10 mm thick slices were cut in a machine with a rotating knife. Potatoes were neither peeled nor blanched.

Drying experiments were performed in a tunnel equipped with electronic balance, pitot tubes for control of air velocity, hygrometer and temperature control (see Fig. 1).

Weight was registered every 42 s and an average of seven measurements stored in the computer. Smoothing of drying-rate curves was by an exponential smoothing procedure according to Jiang (1984) (see Fig. 2).

An apparent diffusion coefficient, D , was calculated from the simplified solution of the diffusion equation for a slice:

$$\ln \left[\frac{W - W_e}{W_0 - W_e} \right] = -\frac{\pi^2 \theta}{4l^2} D$$

where W is moisture content (g water per g dry solid), W_e is water content when equilibrium is reached, W_0 is critical water content, l is thickness of the slice, θ is time, and D is apparent diffusivity. D is slope of the curves in Figs. 3, 4 and 5.

It was assumed that changes in temperature and relative humidity of the drying air did not influence the shrinkage behaviour of the slices. Figures 6

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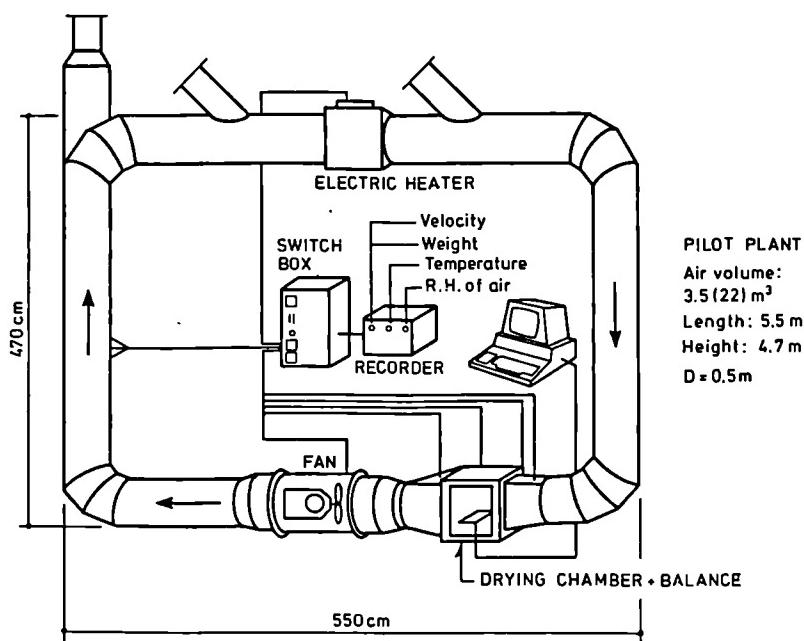


Fig. 1. Sketch of the drying equipment used in the experiments.

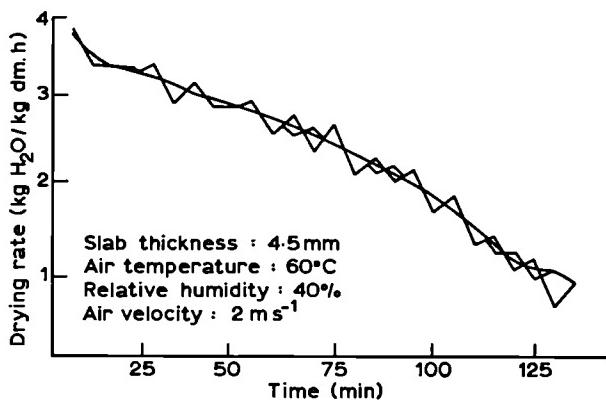


Fig. 2. Three-step smoothing of drying-rate curves.

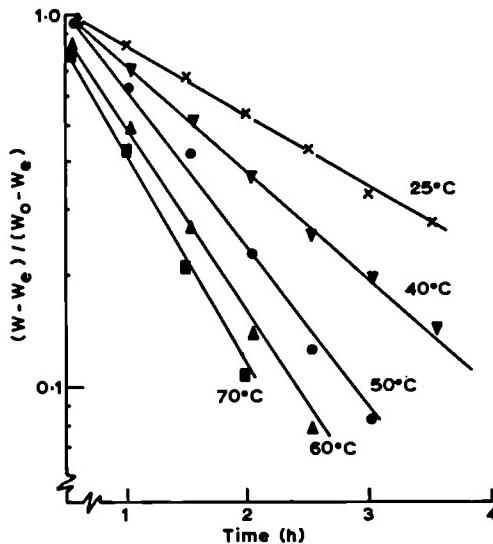


Fig. 3. Moisture change as a function of time and temperature. Relative humidity, 30%; air velocity, 2 m s^{-1} ; slice thickness, 4.5 mm.

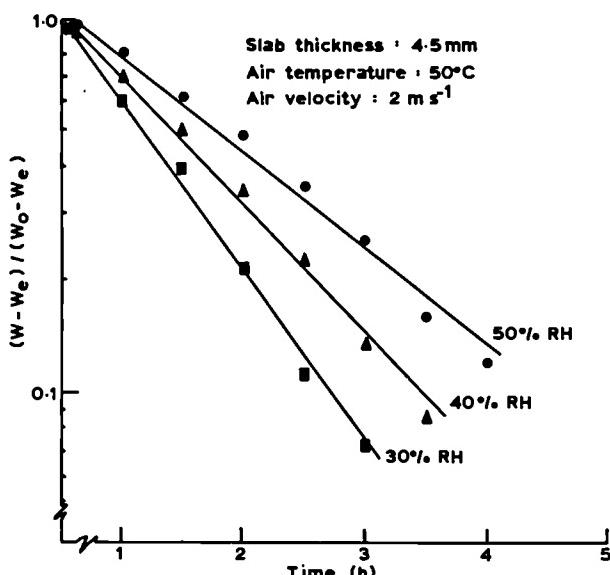


Fig. 4. Moisture change as a function of time and relative humidity of the air.

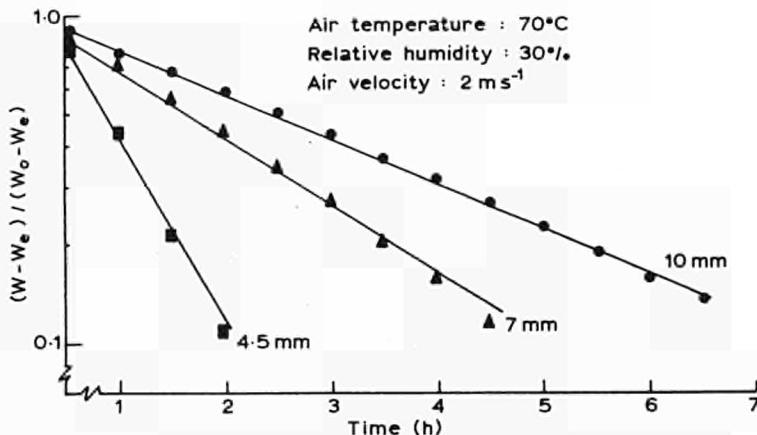


Fig. 5. Moisture change as a function of time and slice thickness.

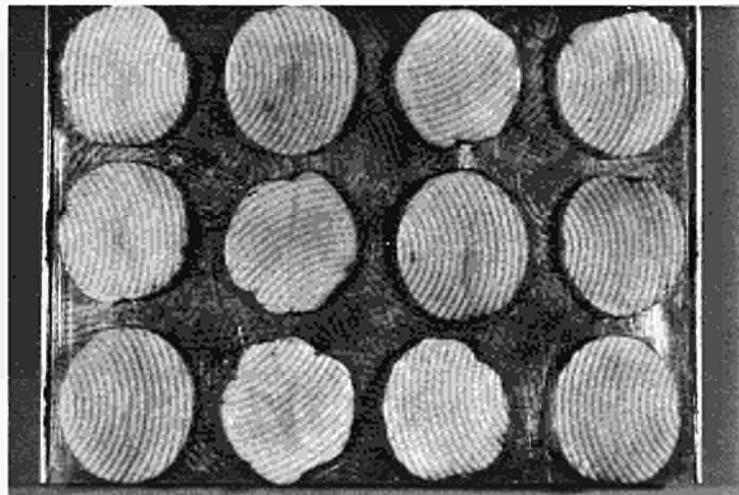


Fig. 6. Potato slices before drying.

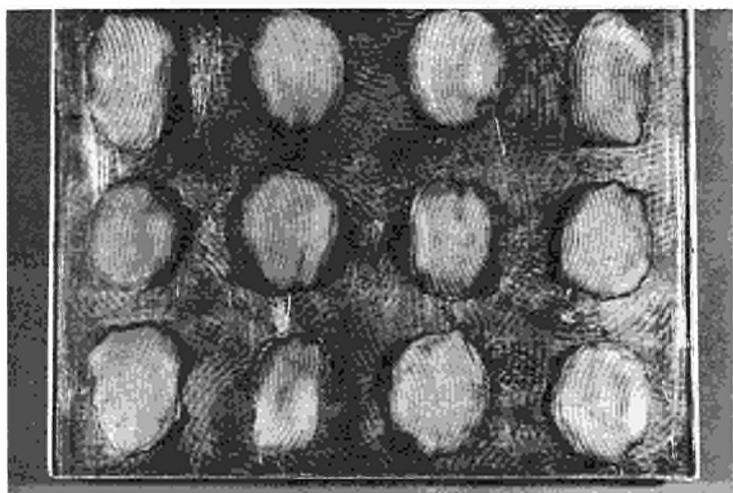


Fig. 7. Potato slices after drying. Shrinkage, bending and cracking have occurred.

and 7 illustrate slices before and after drying. It can be seen that, in addition to shrinkage, bending and cracking will affect drying performance. Results from Fig. 3 are used in an Arrhenius plot, and energy of activation is calculated and compared with some data from the literature (see Fig. 8 and Table 1).

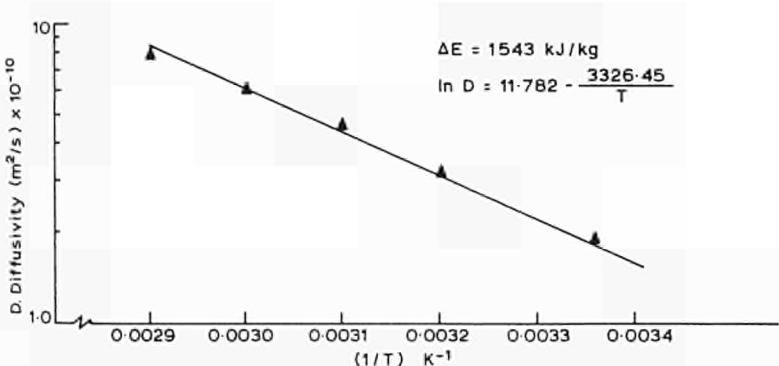


Fig. 8. Arrhenius plot for water diffusivity in drying of potato slices. D is calculated from Fig. 3.

TABLE 1

<i>Product</i>	<i>Energy of activation (ΔE)</i> ($kJ kg^{-1}$)	<i>Reference</i>
Potato slices	1 543	Present investigation
Potato slices	1 784	Islam, E. U. (1980). Ph.D. thesis, Royal Veterinary and Agricultural University, Copenhagen
Potato slices	2 910	Saravacos, C. D. and Charm, S. E. (1962). <i>Fd Technol.</i> , 16 , 78
Potato starch	2 280	Fish, B. P. (1958). <i>Soc. Chem. Ind.</i> , 143-57
Carrots	1 314	Mulet, A., Roselló, C., Piñaga, F., Carbonell, J. V. and Berna, A. (1983). <i>Rev. Agroquim. Tecnol. Aliment.</i> , 23 , 369-77
Sugar beets	1 600	Vaccarezza, L. M., Lombardi, J. L. and Chirise, J. (1974). <i>J. Fd Technol.</i> , 9 , 317-27

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Jiang, T. (1984). *Data Analyses for Chemical Scientists and Engineers*, Chemical Industry Publishers, Beijing.

Determination of the Apparent Diffusion Coefficient of Sodium Chloride in Model Foods and Cheese

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SUMMARY

The results of the COST 90bis work on salt (sodium chloride) diffusion in foods are described. An experimental method for measuring solute diffusion in agar gels has been tested and used to determine the extent of agreement between the results of simple diffusion measurements obtained in different laboratories. The diffusion of salt in agar gel cylinders has been studied in six laboratories for an initial 1% concentration difference at 25°C. The diffusivity was determined from uni-directional diffusion between a gel cylinder containing an initially uniform salt concentration into a contiguous salt-free gel cylinder or one containing a lower concentration. The diffusion coefficient was determined from each experiment by a computerised fitting procedure and by a simple graphical method. The repeatability of the measurements within a laboratory was about 10% (relative standard deviation). Significant differences were observed between the results of different laboratories. The overall average value of the diffusion coefficient was $1.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. In two laboratories the influence of temperature on the diffusion of salt was investigated in the range 5–30°C. Activation energies of $16\text{--}20 \text{ kJ mol}^{-1}$ were obtained from these results.

Based on the collaborative experiments with agar gels, a miniaturised experimental method for diffusion measurements in cheese was developed. It

was used for measuring the penetration of salt in hard cheese in the temperature range 7–20°C. The technique can be adapted easily for investigating other diffusing solutes and other foods.

NOMENCLATURE

C	solute concentration (Cl^- in the case of salt) (kg m^{-3} or % w/w)
C_0	initial solute concentration in the food (eqns. (3) and (7)) or in the first cylinder (eqn. (13)) (kg m^{-3})
C_1	concentration outside the food (eqns. (3) and (7)), or in the second cylinder (eqn. (13)) or in the first mixed cell (eqn. (15)) (kg m^{-3})
C_2	concentration in the second mixed cell (eqns. (15) and (20)) (kg m^{-3})
$C_{1,0}$	initial concentration of solute in the two cells (kg m^{-3})
$C_{2,0}$	
Crit	criterion, minimised sum of squares
C_s	concentration in the food between the two cells (kg m^{-3})
D	apparent or effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
D_1	apparent diffusion coefficient obtained from eqn. (13) by one coefficient identification ($\text{m}^2 \text{s}^{-1}$)
D_3	apparent diffusion coefficient obtained from eqn. (13) by three coefficient identification ($\text{m}^2 \text{s}^{-1}$)
D_m	mean apparent diffusion coefficient obtained from the diffusion values calculated for each of the experimental points by eqn. (13) ($\text{m}^2 \text{s}^{-1}$)
D_t	apparent diffusion coefficient obtained from eqn. (14) (graphical procedure) ($\text{m}^2 \text{s}^{-1}$)
E	apparent activation energy for diffusion (kJ mol^{-1})
Fo	Fourier number
h	sample thickness (m)
L	sample length (m)
M	mass of solute in the food per unit of exposed surface (kg m^{-2})
M_0	initial mass of solute in contact with the exposed surface of the food (kg m^{-2})
N	number of experiments
n	number of terms identified
R	ideal gas constant ($\text{J mol}^{-1} \text{°C}^{-1}$)
s_D	standard deviation of D ($\text{m}^2 \text{s}^{-1}$)
S	surface exposed to solute (m^2)
t	time (s)

T	temperature ($^{\circ}\text{C}$)
V	volume of cells (m^3)
x	distance in the direction of diffusion (m)
x_0	distance at the intercept of the tangent at the inflection point, with the axis $C = C_0$ (eqn. (13)) (m)
x_p	penetration distance (m)

INTRODUCTION

Diffusive migration of small and large molecule solutes during processing and storage determines to a great extent the quality of many foods. In these cases there is a need for quantitative information about the associated diffusion processes. Examples are the curing and smoking of meat, the extraction of sugars and fats, the brining of cheese and vegetables, and the migration of residues from packaging materials or of toxins from micro-organisms on the product surface.

Diffusive migration in foods usually occurs slowly. For example, the curing of meat can take several weeks¹ and equilibration times for cheese range from about 1 to 2 weeks in soft cheese to several months in semihard cheese.²⁻⁸ In Parmesan cheese, which represents an extreme case, salt equilibrium is only attained after about 10 months.⁴ For the controlled manufacture of these products, it is therefore important to know the factors influencing salt penetration and to be able to predict the diffusion rates. This implies knowledge of the apparent diffusion coefficient and its dependence on factors such as temperature and concentration.

For foodstuffs with a heterogeneous structure, it is often difficult to know exactly the volume into which the solute can penetrate and the path of migration. Nevertheless, the movement of solutes can adequately be described as a diffusion process using an apparent or effective diffusion coefficient.^{9,46}

The main purpose of this study was to obtain information about the repeatability and reproducibility of measurements of the apparent diffusion coefficient. A collaborative study was undertaken using a simple model system consisting of agar cylinders of different salt concentrations. In addition, a comprehensive bibliography on migration of salt in foods was prepared. Finally, the experimental method used in the collaborative work was modified and adapted in one laboratory for studying salt diffusion in a real food—cheese—and the effect of temperature on the salt penetration in the cheese was measured.

BIBLIOGRAPHY ON SALT DIFFUSION IN FOODS

A bibliography related to the diffusion and analysis of salt in foods was prepared and served as a basis for the work of the Diffusion Properties Subgroup.¹⁰ The bibliography contains a comprehensive list of literature dealing with penetration of salts into foods. The emphasis throughout was on sodium chloride but other low molecular weight solutes were also considered. Because the penetration of salts into foods is in most cases accompanied by a counterflow of water, some references with data on its diffusion properties are also incorporated. Primary literature (scientific papers describing original research results) as well as reviews, conference literature and some important books were included. Four tables have been added to the bibliography showing values of the diffusion coefficient of sodium chloride and other solutes in cheese, meat and other systems of interest in food processing. Copies of the bibliography, which contains more than 200 references, are available on request from the authors.¹⁰

MATHEMATICAL MODELS AND DIFFUSION EQUATIONS

Various experimental techniques and appropriate mathematical treatments have been proposed to obtain apparent diffusion coefficients in foods.¹¹ They can be classified into two main groups:

- (a) non-steady state diffusion through a thick layer of food; and
- (b) diffusion through a thin slice of food acting as a membrane and separating two perfectly mixed cells.

In the first group the end of a cylindrical or parallelepiped-shaped sample of the food is brought into contact with the pure or dissolved diffusant or with another cylinder of food containing a different concentration of the solute.

The diffusion process obeys Fick's second law of diffusion:¹²

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

The solution of this equation depends on the experimental conditions. When the solid material, initially free from solute, is brought into contact with solute, maintained at a constant concentration C_1 at the interface, the

boundary conditions are as follows:

$$\begin{aligned} t = 0 & \quad C = C_0 \\ x = 0 & \quad C = C_1 \quad \text{for } t > 0 \\ x \rightarrow \infty & \quad C = C_0 \quad \text{for } t > 0 \end{aligned}$$

A further condition corresponds to the fact that the duration of the experiments is assumed to be such that the solute does not reach the extremity of the foodstuff. The solid is thus considered as a semi-infinite medium; the validity condition of this limiting condition is that the Fourier number $Fo = Dt/L^2$ be less than 0·05 where L is the length of the solid along the x axis.

The solution of eqn. (1) is then

$$C(x, t) = C_1 \operatorname{erfc} \left(\frac{x}{\sqrt{(4Dt)}} \right) \quad (2)$$

and if $C_0 = 0$

$$\frac{C - C_0}{C_1 - C_0} = \operatorname{erfc} \left(\frac{x}{\sqrt{(4Dt)}} \right) \quad (3)$$

It is possible from this relationship to calculate the quantity M of solute which has penetrated the solid in a time t per unit of exposed surface:

$$M = 2C_1 \left(\frac{Dt}{\pi} \right)^{0.5} \quad (4)$$

This is valid provided $Fo < 0\cdot05$.

It is also possible to define a penetration distance x_p as the distance for which, in a time t , the change in concentration is 1%, for example of C_1 . This gives the rate of advance of the boundary at $0\cdot01C_1$.

$$x_p = 3\cdot64 \sqrt{(Dt)} \quad (5)$$

If $Fo > 0\cdot05$, i.e. if the assumption of a semi-infinite medium no longer applies, the last boundary condition must be changed. This is what happens during migration when the salt reaches every part of the solid. The conditions now are

$$\begin{aligned} t = 0 & \quad C = C_0 \\ x = 0 & \quad C = C_1 \quad \text{for } t > 0 \\ x = L & \quad \frac{\partial C}{\partial x} = 0 \quad \text{for } t > 0 \end{aligned}$$

and the solution is given by

$$\frac{C - C_0}{C_1 - C_0} = 2 \sum_{n=0}^{\infty} \frac{(-1)^n}{(n + \frac{1}{2})\pi} \exp \left[-(n + \frac{1}{2})^2 \pi^2 \frac{Dt}{L^2} \right] \times \cos \left[(n + \frac{1}{2})\pi \frac{x}{L} \right] \quad (6)$$

This solution is often given graphically.¹²

The experimental conditions are different when the foodstuff and a fixed quantity M_0 of solute are brought into contact. The boundary and initial conditions are

$$\begin{aligned} t &= 0 & C &= C_0 \quad \text{for } x > 0 \\ x &\rightarrow \infty & C &= C_0 \quad \text{for } t > 0 \\ M &= M_0 = \int_0^{\infty} C dx & & \quad \text{for } t > 0 \end{aligned}$$

at the beginning of the diffusion process, when the medium can be considered as semi-infinite. When this is not possible,

$$x = L \quad \frac{\partial C}{\partial x} = 0 \quad \text{for } t > 0$$

The solution to eqn. (1) is then as follows:¹²

$$C = \frac{M_0}{\pi Dt} \exp(-x^2/4Dt) \quad (7)$$

for the semi-infinite case, and for the finite case:

$$C = \frac{M_0}{\pi Dt} \left\{ \exp(-x^2/4Dt) + \sum_{i=1}^{\infty} \left[\exp\left(\frac{-(2iL+x)^2}{4Dt}\right) + \exp\left(\frac{-(2iL-x)^2}{4Dt}\right) \right] \right\} \quad (8)$$

The boundary conditions for uni-directional diffusion from a semi-infinite food cylinder containing an initially uniform concentration of the

diffusing substance into a contiguous semi-infinite cylinder free of solute or containing a lower concentration¹⁴ are

$$\begin{aligned}
 t = 0 & \quad C = C_1 & \text{for } x < 0 \\
 & \quad C = C_0 & \text{for } x > 0 \\
 & \quad C|_{x=0^-} = C|_{x=0^+} & \text{for } t > 0 \\
 & \quad \frac{\partial C}{\partial x}\Big|_{x=0^-} = \frac{\partial C}{\partial x}\Big|_{x=0^+} & \text{for } t > 0 \\
 x \rightarrow \infty & \quad C = C_1 & \text{for } t > 0 \\
 x \rightarrow -\infty & \quad C = C_0 & \text{for } t > 0
 \end{aligned}$$

The solution of eqn. (1) in this case is

$$\frac{C - C_0}{C_1 - C_0} = \frac{1}{2} \left(1 - \operatorname{erfc} \frac{x}{\sqrt{4Dt}} \right) = \frac{1}{2} \operatorname{erfc} \left(\frac{x}{\sqrt{4Dt}} \right) \quad (9)$$

provided the semi-infinite assumptions are fulfilled.

In the case of experiments corresponding to eqns. (4), (5) and (9) a simple graphical solution is possible:

- eqn. (4): M is plotted against \sqrt{t} ; a straight line passing through the origin is obtained, with a slope of $2C_1(D/\pi)^{1/2}$.
- eqn. (5): the increase x_p is plotted versus \sqrt{t} .
- eqn. (7): the sample is cut up into thin slices assumed to be homogeneous and the concentration is measured. For a given time $\ln C$ is plotted against x^2 . The slope is equal to $-1/4Dt$.
- eqn. (9): the equation of the tangent at the inflection point of the sigmoid curve is given by

$$C = \frac{C_1 + C_0}{2} - \frac{C_1 - C_0}{2\sqrt{\pi Dt}} x$$

and the intercept with the axis $C = C_0$ is^{14,15}

$$x_0 = (\pi Dt)^{1/2} \quad (10)$$

In the other cases, the value of D is determined from concentration profiles by minimisation of the sum of the squares of the deviations between

the observed (C_{exp}) and calculated values (C_{cal}). The minimum of the criterion

$$\text{Crit} = \sum_{i=1}^N (C_{\text{exp}} - C_{\text{cal}})^2$$

is obtained by the classical golden number section method.

In the second group of methods, a thin slice of food is used as a porous membrane separating two perfectly mixed cells with initially different solute concentrations. Assuming quasi-steady state diffusion through the slice (surface area S , thickness h) the mass balance between the two cells 1 and 2 is given by

$$V_2 \frac{dC_2}{dt} = \frac{DS(C_1 - C_2)}{h} , \quad -V_1 \frac{dC_1}{dt} = \frac{DS(C_1 - C_2)}{h} \quad (11)$$

When $C_{2,0}$, the concentration of the solute at $t=0$, is zero and when V_1 equals V_2 , the concentration in the second cell is given by

$$\ln\left(\frac{C_{1,0} - 2C_2}{C_{1,0}}\right) = -\frac{2}{V_2} \frac{DS}{h} t \quad (12)$$

When the duration of the experiment and choice of initial values for C_1 and C_2 are such that C_2 remains small compared with $C_{1,0}$, the solution reduces to

$$C_2 = \frac{DC_{1,0}S}{V_2 h} t \quad (13)$$

and D is obtained directly from the slope of C_2 versus time.

If the quasi-steady state assumption within the slice is not valid, the concentration in the membrane is given by Fick's second law:

$$\frac{\partial C_s}{\partial t} = D \frac{\partial^2 C_s}{\partial x^2} \quad (14)$$

with the boundary or initial conditions:

$$\begin{aligned} t = 0 & \quad C_s = C_{s0} \\ x = 0 & \quad C_s = C_1 = C_{1,0} \quad \text{for } t > 0 \\ x = h & \quad -SD \frac{\partial C_s}{\partial x} \Big|_{x=h} = V_2 \frac{dC_s}{dt} \quad \text{for } t > 0 \end{aligned}$$

The solution of eqn. (14) then leads to the expression for the time course of the solute concentration in the second cell with the lower initial concentration:¹⁶

$$\frac{C_2 - C_{2,0}}{C_{1,0} - C_{2,0}} = 1 - \sum_{n=0}^{\infty} \frac{2(\alpha_n^2 + a^2)}{\alpha_n^2 + a^2 + a} \frac{\sin \alpha_n}{\alpha_n} \exp\left(-\frac{D\alpha_n^2 t}{h^2}\right) \quad (15)$$

In this expression $a = hS/V_2$ is a dimensionless number and the α_n are the roots of

$$\alpha \tan \alpha = a \quad (16)$$

For small values of a and after a sufficient time, all the exponential terms except the first for $n=0$ become zero. Equation (15) then reduces to the form of eqn. (13), provided $C_0 = 0$.

The methods of the first group have been used more frequently during the past because fewer experimental difficulties are involved and more reliable results are obtained for heterogeneous materials. The Diffusion Properties Subgroup chose the touching semi-infinite cylinders technique for its collaborative work mainly because of the simple experimental requirements and the possibility of obtaining the apparent diffusion coefficient by both a graphical method (eqn. (10) and a mathematical procedure which takes into account the whole concentration profile (eqn. (9). A third reason for the choice was the possibility of adapting the technique to other systems, including real foods.

COLLABORATIVE STUDY WITH AGAR GELS

Experimental Procedure

An experimental procedure similar to that proposed by Naesens *et al.*¹⁵ was used to measure the diffusion of salt in 3% agar gel. The experiments were performed at 25°C. Salt concentration was usually determined after 6 h by chloride titration as a function of the distance of penetration.

Reagents

- Agar-agar powder (Merck, No. 1615) and agarose (Litex agarose LsL for gel electrophoresis).
- Sodium chloride (Merck a.r.).

Apparatus

- Glass cylinders for containing the gel cylinders: 150 mm length, 12 mm internal diameter, with a mark on the glass surface at the 75 mm length.
- Glass rod closely fitting inside the glass cylinders.
- Glass jars of about 100 cm³ capacity (for preparation of gels) with hermetic lids.
- Small glass tubes or jars of about 10 cm³ capacity with hermetic lids (for salt concentration determination).
- Incubator at 25 ± 0.5°C or thermostatically-controlled room.

Preparation of gels

3 g of agar (for the lower half of the diffusion cylinder) and 3 g of agar + 1 g of sodium chloride (for the upper part) are dispersed and made up to 100 g, each with distilled water (or the appropriate salt solution). Glass jars are filled with each mix and closed. The mix is then allowed to stand for about 16 h at ambient temperature and then heated for 20 min in a boiling water bath. Stirring during heating is made by frequent but not too vigorous 'end over end' shaking.

After cooling to about 50°C, the upper half of the agar solution, liable to contain air bubbles, is discarded. The remaining solution is used to fill the lower half of one of the glass cylinders. When this lower half has gelled it is pushed along so that its free surface just protrudes from the end of the glass cylinder and can be cut with a razor blade in order to provide a smooth, flat surface, orthogonal to the axis. A second gel column (using a second glass cylinder) is prepared in the same way containing the diffusant (e.g. 1% sodium chloride).

The two gel cylinders are then fused together in one glass cylinder with a drop of distilled water between the mating faces and the junction is pushed back to the mark in the middle of the glass cylinder. The cylinder is closed with plastic stoppers and stored at 25 ± 0.5°C.

Because of difficulties in preparing bubble-free gels containing more than 3% salt some laboratories modified the technique slightly, as follows. 3 g of agar (or agarose) and the appropriate quantity of salt were weighed and made up to 100 g with distilled water. Glass beads or boiling stones were added and the dispersion was heated on an oil-bath in a round-bottom flask under reflux. The temperature of the oil-bath was maintained at around 120°C. After about 3 h a clear bubble-free solution is formed. After removing any thin film on the surface, the solution was transferred to the glass cylinders for the diffusion experiments.

Determination of concentration profiles

After 6 h of diffusion the gel cylinders are pushed from the glass tubes by means of the glass rod and cut into about 24 slices (12 on each side of the junction) of about 1.5 mm thickness, using a razor blade. Each slice is weighed in the small glass tubes, 2–3 ml of water is added and the tubes are closed. The amount of salt present in each sample is determined using the appropriate analytical method. The salt concentration in each slice is then calculated and plotted against the distance, x , of the slice from the junction. The distance is assessed from the position and weight of each slice.

Calculation of diffusivity

For each experiment, the diffusivity is obtained from eqn. (9) using a non-linear regression procedure as described in the preceding section or graphically using eqn. (10).

Participating Laboratories

The six laboratories which took part in the collaborative study are listed in Table 1. Seven sets of independent results were obtained from these laboratories. Preliminary experiments showed that results obtained with agarose and agar did not differ significantly.

Results

A total of 105 experiments were considered despite deviations in some from the standard experimental procedure. The most important experimental conditions are summarised in Table 2.

Calculation of the Apparent Diffusion Coefficient

The experimental data for each experiment consisted of a set of chloride concentrations as a function of the distance from the contact zone. The apparent diffusion coefficient was estimated using four different methods.

1. For each experiment the following sum of squares was minimised:

$$\text{Crit} = \sum_{i=1}^N (C_{\text{exp}} - C_{\text{cal}})^2$$

where N = number of concentration measurement, C_{exp} = experimental chloride concentration, and C_{cal} = calculated chloride concentration using eqn. (9).

TABLE 1
NAMES AND ADDRESSES OF PARTICIPATING LABORATORIES

Federal Dairy Research Institute
 Biophysics Section
 CH-3097 *Liebefeld-Bern*
 Switzerland

National Technical University
 Department of Chemical Engineering, Laboratory of Unit Operations
 GR-106 82 *Athens*
 Greece

Bundesforschungsanstalt für Ernährung
 Engesserstrasse 20
 D-7500 *Karlsruhe 1*
 Federal Republic of Germany

Université de Clermont 2
 Laboratoire de Génie Chimique Biologique
 BP45
 F-63170 *Aubière*
 France

ENSAIA
 Laboratory of Physical Chemistry and Food Engineering
 2 avenue de la Forêt de Haye
 F-54500 *Vandoeuvre les Nancy*
 France

Experimental Station for the Food Preservation Industry
 Viale Tanara 31/A
 I-43100 *Parma*
 Italy

The minimum of Crit was obtained using a Gauss-Newton method. The error function in (9) was calculated as a series of exponential terms. The diffusion coefficient obtained is designated D_1 . C_0 and C_1 are the measured concentrations at the ends of the cylinders remote from the junction.

2. The coefficient was obtained as above but three quantities D , C_0 and C_1 were simultaneously adjusted. The experimental values of C_0 and C_1 were not always known accurately and it was noted that the model is sensitive to these variables. The diffusion coefficient thus obtained is designated D_3 , because 3 variables were adjusted. These two procedures were applied to all data sets using a Hewlett-Packard model HP-87 microcomputer and a BASIC program, which is available on request from

TABLE 2
EXPERIMENTAL CONDITIONS

Laboratory (coded name)	Number of experiments	Initial salt concentrations in the two cylinders (C_1/C_0 (% w/w))	Agar concentration (% w/w)	Temperature (°C)	Diffusion time (h)	Chloride determination method
GR	3	1/0	3	25	6	Specific Cl electrode. Ingold 157 203 and reference electrode 10 303 3048
HA	5	1/0	3	25	6	Specific Cl electrode. Ingold 157 203 and reference electrode 10 303 3048
	3	5/4	3	25	6	Titration with HgCl_2
RU	11	1/0	3	25	6	Sigma Diagnostics Procedure No. 830
	4	2/1	3	25	6	(14 h for 3 exp.)
	3	3/2	3	25	6	
	6	5/4	3	25	6	
	5	1/0	3	25	6	Titration with HgCl_2
PA	5	11/10	3	25	6	Sigma Diagnostics Procedure No. 830
	5	1/0	3	25	6	Titration with HgCl_2
GD	2	1/0	3	25	6	Sigma Diagnostics Procedure No. 830
CH	5	1/0	2	25	6	Titration with HgCl_2
	2	1/0	3	25	6	Sigma Diagnostics Procedure No. 830
ST	5	1/0	1	25	6	Titration with HgCl_2
	8	1/0	2	25	6	Sigma Diagnostics Procedure No. 830
	6	1/0	3	25	6	
	8	1/0	5	25	6	
	4	1/0	7	25	6	
	6	1/0	3	5	6	
	7	1/0	3	18.5	6	
	6	1/0	3	30	6	

the authors. The quality of the fit was judged by the mean standard deviation around the regression curve:

$$\text{MSD} = \sqrt{\text{Crit}/(N(N-n))}$$

Examples of the output are in the Appendix.

3. The coefficient was calculated for each experimental concentration measured on both sides of the contact zone using eqn. (9). Generally only the central 80–90% of the final concentration range was considered. Obvious outliers were eliminated and an average coefficient, D_m , was calculated for each experiment.

4. The coefficient was estimated graphically from the tangent at the point of inflection of the experimental concentration–distance curve using eqn. (10). The symbol D_t is used for these values.

Typical examples of experimental and calculated concentration curves are shown in Fig. 1. The corresponding data are given in the Appendix. Both calculated curves, obtained by adjusting either one (D_1) or three variables (D_3 , C_0 and C_1), fit the experimental points well. However, the values of D_1 and D_3 are slightly different in most experiments, probably because of the sensitivity of the model to the values of C_0 and C_1 .

The advantage of the graphical procedure is that only a few points around the contact zone need be determined and that C_0 and C_1 need not be known. However, this method can give unreliable results if the experimental points near the contact zone are not precise enough.

The values of the apparent diffusion coefficients calculated from the data of the different laboratories are given in Table 3. The extreme values of D were 0.5 and $3.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The four methods of calculation sometimes lead to significantly different values. The differences were generally most pronounced if C_0 and C_1 could not be determined with great accuracy and if the standard deviations of the individual D -values were large.

Statistical Analysis of the Results

The results of the collaborative study were tested for inhomogeneities of variances and differences between mean D -values within and between laboratories. The following statistical tests were applied:

- test for normality of repeated measurements;
- Bartlett's χ^2 statistic for test of homogeneity of variances;
- Fischer or t -statistic for testing differences between mean values; and
- test according to Newman and Keuls for comparison of means from different laboratories.

TABLE 3

RESULTS OF COLLABORATIVE STUDY: APPARENT DIFFUSION COEFFICIENTS FOR SODIUM CHLORIDE IN AGAR GELS AT 25°C ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)

<i>Laboratory (coded name)</i>	<i>Initial NaCl concentrations (C_1/C_0 (% w/w))</i>	<i>Agar concentration (% w/w)</i>	<i>D₁</i>		<i>D₃</i>		<i>D_m</i>		<i>D_t</i>	
			<i>D₁</i>	<i>s_D</i>	<i>D₃</i>	<i>s_D</i>	<i>D_m</i>	<i>s_D</i>	<i>D_t</i>	<i>s_D</i>
GR	1/0	3	1.35	0.33	1.31	0.22	—	—	1.45	0.32
HA	1/0	3	1.62	0.25	1.89	0.29	1.35	0.10	—	—
	5/4	3	1.49	0.40	1.31	0.63	1.61	0.07	—	—
RU	1/0	3	1.67	0.25	1.63	0.22	1.66	0.24	1.74	0.34
	2/1	3	1.68	0.09	1.62	0.10	1.61	0.14	1.51	0.28
	3/2	3	1.45	0.39	1.29	0.28	1.87	0.48	1.35	0.22
	5/4	3	2.14	0.67	1.94	0.49	2.75	1.30	1.90	0.51
PA	1/0	3	1.12	0.14	3.57	2.20	1.83	0.74	—	—
	11/10	3	0.55	0.17	1.06	0.37	0.87	0.31	—	—
GD	1/0	3	1.18	0.06	1.11	0.11	1.18	0.02	—	—
CH	1/0	2	1.61	0.07	1.42	0.21	1.48	0.13	—	—
	1/0	3	1.54	0.01	1.48	0.16	1.47	0.01	—	—
ST	1/0	1	1.39	0.08	1.40	0.09	1.34	0.10	—	—
	1/0	2	1.37	0.12	1.44	0.18	1.31	0.11	—	—
	1/0	3	1.29	0.06	1.33	0.11	1.36	0.08	—	—
	1/0	5	1.29	0.09	1.30	0.13	1.32	0.15	—	—
	1/0	7	1.34	0.14	1.34	0.09	1.36	0.08	—	—

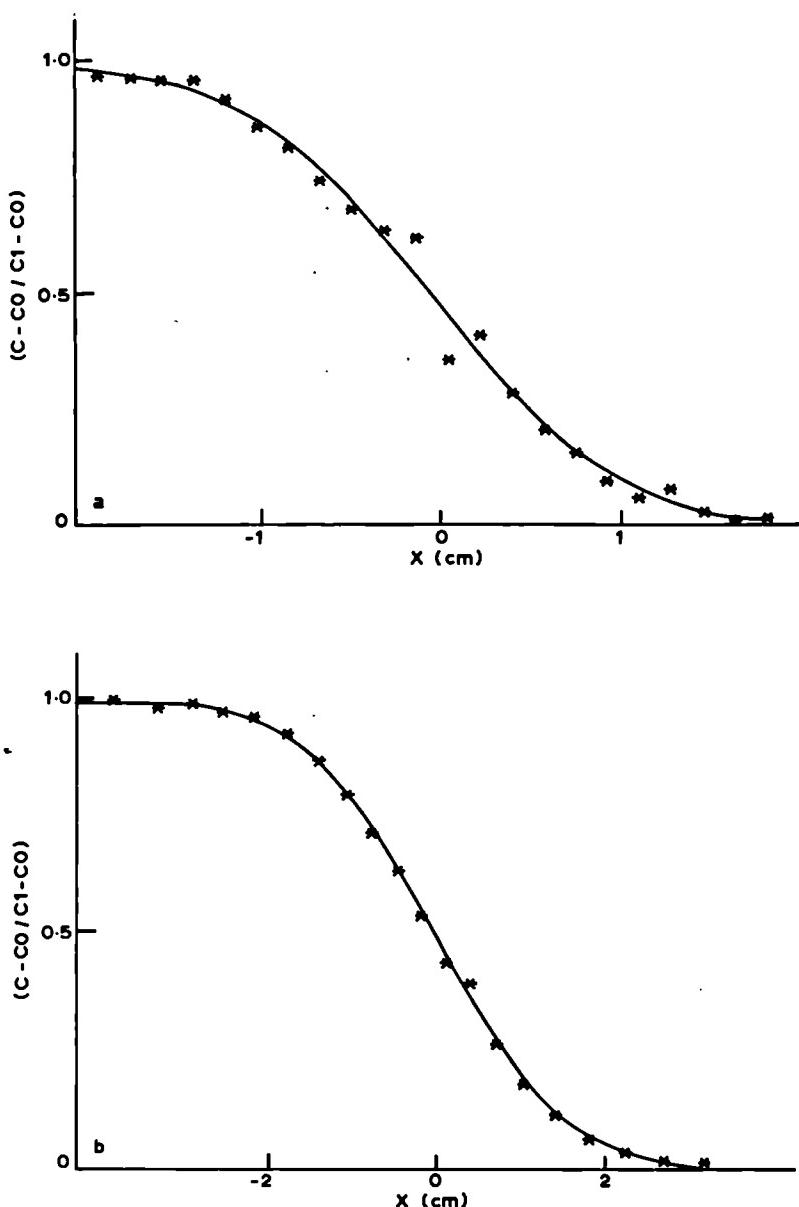


Fig. 1. Examples of calculated concentration curves. (The corresponding experimental data are given in the Appendix. Data from GR (a) and RU (b).)

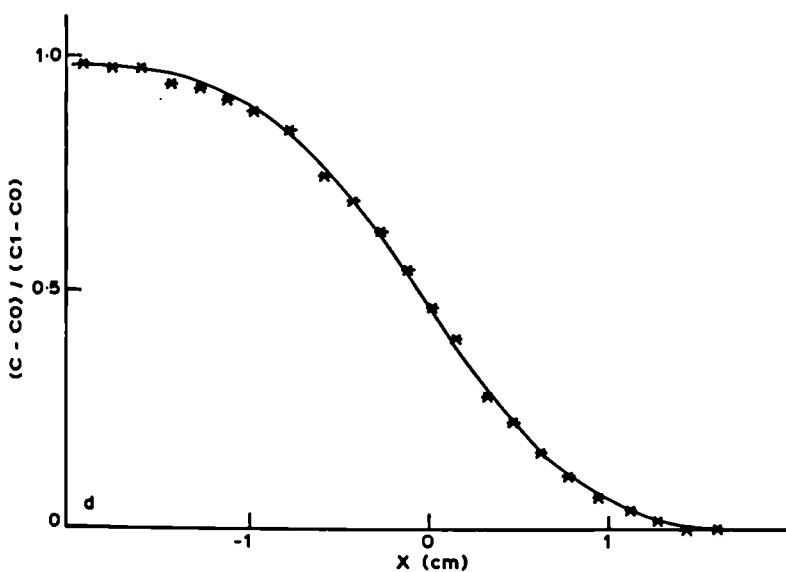
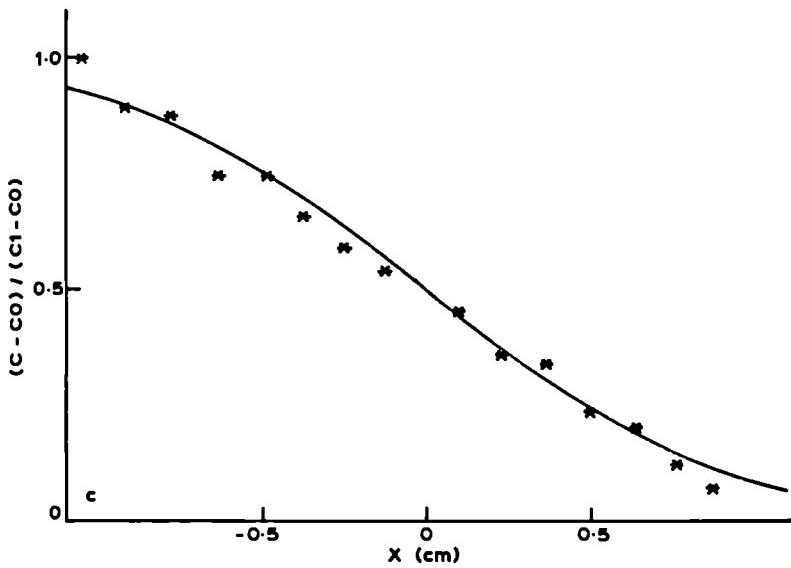


Fig. 1.—contd. Data from PA (c) and GD (d).

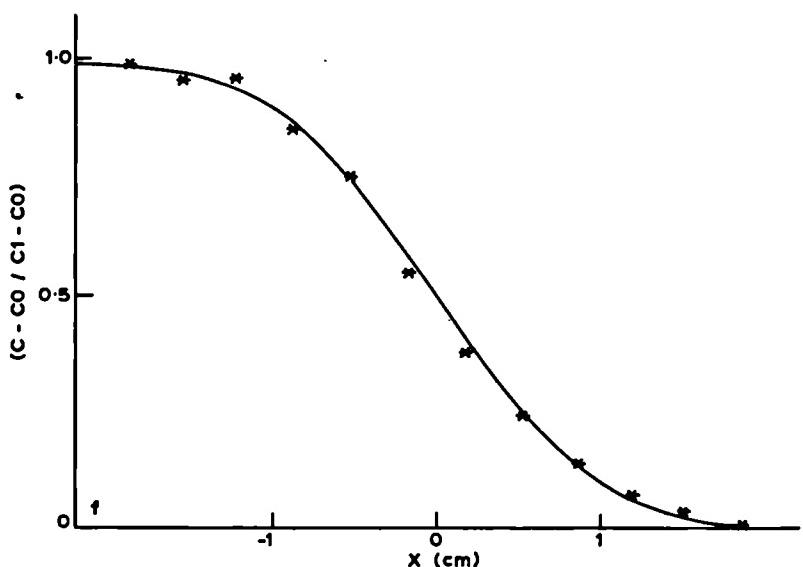
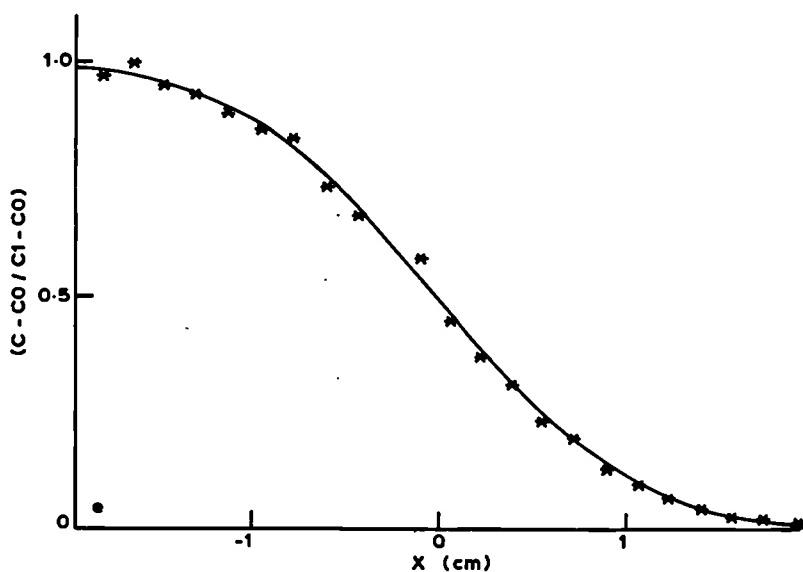


Fig. 1.—*contd.* Data from CH (e) and ST (f).

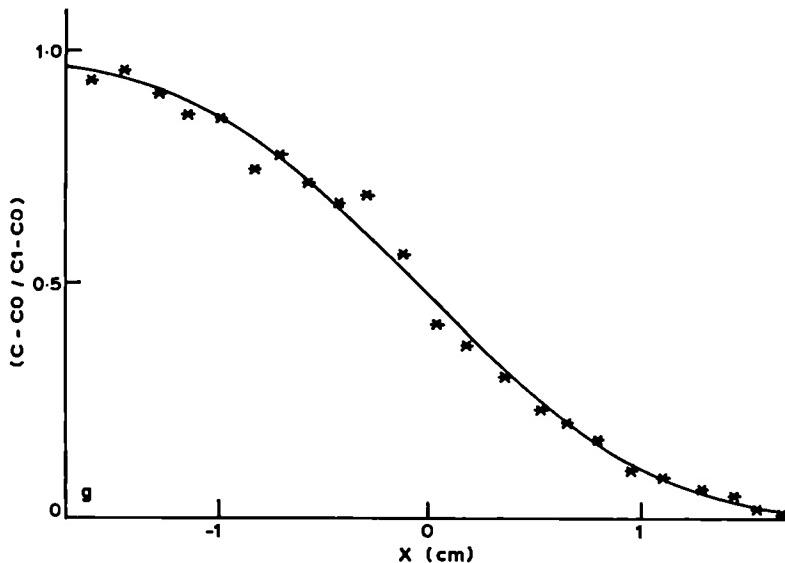


Fig. 1.—contd. Data from HA.

TABLE 4
 STATISTICAL TESTS FOR HOMOGENEITY OF VARIANCES AND DIFFERENCES
 BETWEEN MEAN APPARENT DIFFUSION COEFFICIENTS WITHIN PARTICIPATING
 LABORATORIES

<i>Laboratory</i>	<i>Diffusion coefficients and standard deviations</i> $(10^{-9} m^2 s^{-1})$			
	D_1	s_D	D_3	s_D
RU	1.76 n.s.d.	0.44 n.h.	1.66 n.s.d.	0.35 n.h.
ST	1.33 n.s.d.	0.10 h.	1.37 n.s.d.	0.14 h.
CH	1.59 n.s.d.	0.07 h.	1.43 n.s.d.	0.18 h.
HA	1.57 n.s.d.	0.29 h.	1.68 n.s.d.	0.50 h.
PA	s.d.	h.	n.s.d.	n.h.

n.s.d.: no significant differences within laboratory.

s.d.: significant differences within laboratory.

n.h.: variances not homogeneous.

h.: variances homogeneous.

The main results of the statistical analysis are summarised in Table 4. Only the D_1 - and D_3 -values, which were calculated by the same procedure for all experiments, have been considered. From the analysis of the results of ST and CH, it may be concluded that the apparent diffusion coefficients did not depend on the agar concentration in the range 1–7%. Similarly, the statistical analysis of the results obtained by RU and HA suggest that the D -values did not depend on the initial salt concentration, which ranged from 1 to 5%.

The median (used because of its relative robustness and insensitivity to outliers) of all D_1 -values was $1.39 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. It was not significantly different from that of the D_3 -values, which was $1.40 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The average relative standard deviation was 10% for D_1 and 15% for D_3 .

The Bartlett test revealed that the variances were not homogeneous in certain laboratories (PA) or for some series of experiments (RU 5/6). It was decided, therefore, to discard the corresponding values. A Fischer test was applied to the remaining data. It indicated significant differences between the D -values obtained in the various laboratories. The Newman and Keuls statistical test suggested the existence of two subgroups:

- | | |
|--------------------|---|
| (1) RU, ST, CH | $D_1 = 1.46, s_D = 0.22 (10^{-9} \text{ m}^2 \text{ s}^{-1})$ |
| | $D_3 = 1.44, s_D = 0.20 (10^{-9} \text{ m}^2 \text{ s}^{-1})$ |
| (2) CH, ST, GD, GR | $D_1 = 1.37, s_D = 0.15 (10^{-9} \text{ m}^2 \text{ s}^{-1})$ |
| | $D_3 = 1.36, s_D = 0.16 (10^{-9} \text{ m}^2 \text{ s}^{-1})$ |

The experiments RU 5/4 were not included in the first group.

The relatively poor reproducibility and the possible presence of two groups of D -values indicates that there are some as yet unknown factors which influence to some extent the determination of the apparent diffusion coefficient with this technique. A better standardisation of the experiments could possibly improve repeatability within, and reproducibility between, laboratories. For example, the use of the same method for chloride determination, cutting and weighing of the slices more quickly before chloride analysis and following exactly the same procedure for the preparation of the agar gels.

Although the methods of calculation of D from the concentration-distance curves did not influence the result in most cases, it is recommended that non-linear regression procedures be applied to the results over the whole length of the cylinders. The concentrations C_0 and C_1 in the plateau regions must be determined with the same precision as those near the contact zone because they influence significantly the curve fitting procedure. The time allowed for diffusion should therefore be such as to

ensure a sufficiently long plateau region (say 10%) at the outer end of each cylinder.

The mean D -value obtained in this collaborative study ($D = 1.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) is slightly less than that reported by other authors for sodium chloride at infinite dilution in pure water, $1.612 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Refs. 17-19). They found that the diffusivity of salt in pure water was concentration-dependent. At concentrations increasing from 0.06 to 0.3 and 0.6% w/w, D -values decreased from 1.54 to 1.50 and $1.48 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, respectively. Between 1.2 and 4.5% w/w the values levelled off to about $1.47 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. At higher concentrations D increased again from 1.48 at 5.6 to 1.51 at 10.8% w/w. The diffusion behaviour of salt in agar gels is most probably similar as no significant concentration effect in the concentration range 1-5% salt could be detected. For future collaborative studies, however, the concentration levels 1.0% salt should not be chosen as a reference system because of the steeper slope of the D versus concentration curve in this region.

Influence of Temperature

The influence of temperature was measured by one laboratory (ST) using the same technique between 5 and 30°C. These results were treated to obtain D_1 , D_3 and D_m . Apparent activation energies calculated from the relationship

$$D = D_0 \exp(-E/RT)$$

were 16.0, 19.6 and 13.7 kJ mol⁻¹, respectively (Table 5 and Fig. 2).

TABLE 5
INFLUENCE OF TEMPERATURE ON THE APPARENT DIFFUSION COEFFICIENT OF SODIUM CHLORIDE IN AGAR GEL
(3% agar, 1.0% salt, laboratory ST)

T (°C)	D_1 ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)		D_3 ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)		D_m ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	
	D_1	s_D	D_3	s_D	D_m	s_D
5	0.87	0.10	0.78	0.12	0.91	0.14
18.5	1.19	0.07	1.20	0.08	1.23	0.07
25	1.33	0.10	1.37	0.14	1.36	0.08
30	1.61	0.28	1.61	0.27	1.48	0.05
Activation energy E (kJ mol ⁻¹)	5.30		16.0		19.6	
					13.7	

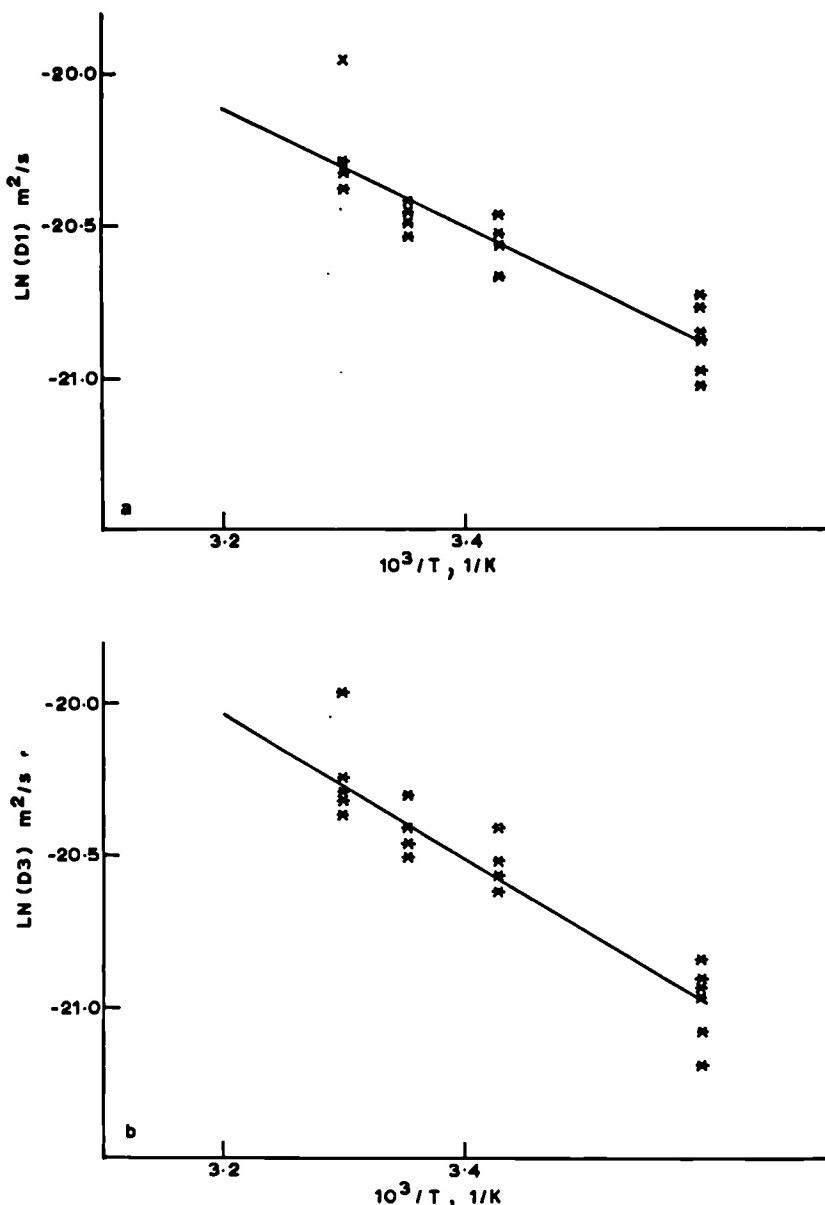


Fig. 2. Arrhenius plot for the apparent diffusion coefficients D_1 (a) and D_3 (b) in the temperature range 5–30°C.

These values may be compared with those obtained by another laboratory (GR) between 5 and 25°C using the diffusion cell technique and eqns. (16) and (14). The activation energies for 5 and 25°C were 19.8 and 18.7 kJ mol⁻¹, respectively. These values are very close to the activation energy for the viscosity of pure water, i.e. 18 kJ mol⁻¹ between 5 and 30°C.

MEASUREMENT OF SALT DIFFUSION IN CHEESE

The importance of both salt concentration and its uniform distribution throughout the curd for the quality of cheese is well known. Salt contributes directly to the cheese flavour, controls the multiplication and metabolism of the micro-organisms, and influences the activity of enzymes as well as the texture of the cheese body and surface.²²⁻⁴⁶ Many effects of salt can be related to the strong influence on water activity (a_w) of the salt concentration in the aqueous phase of cheese.⁴⁷⁻⁵⁶

Most varieties of cheese are salted by immersion in brine or by rubbing dry salt or brine on the surface. Cheddar cheese and some others are salted by adding salt to the milled curd. Direct salting of cheese by jet injection of salt and other curing components has also been described.⁵⁷⁻⁵⁹

Cheeses which are salted by immersion in a brine bath or by surface application require a long time to attain uniform distribution of the salt. Equilibration times range approximately from 1 to 2 weeks in soft cheese to several months in semi-hard and hard cheese.^{2,3-8} In Parmesan cheese, an extreme case, salt equilibrium was attained only after about 10 months.⁴

The theoretical aspects of salt penetration into cheese during and after brine salting have been discussed by several authors.^{23,60-65} In a fundamental study of the penetration of salt into cheese, which is accompanied by an outward migration of water, Geurts *et al.*⁶⁰ defined and determined an apparent diffusion coefficient (D) for salt in cheese moisture. They concluded from their results that the movement of salt in cheese can be properly described as a diffusion process. D was found to be about $2.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 12.6°C, in a full-cream model cheese containing 40–45% water. D -values reported by Geurts *et al.*^{60,61} and other authors^{23,31,65-67} range from about 1.4 to $3.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, depending mainly on water content and temperature but also to some extent on fat-to-non-fat solids ratio,^{60,67} brine composition,^{61,65} proteolysis, calcium content and homogenisation of milk.⁶⁷ pH and brine concentration apparently had no influence on the apparent diffusion coefficient.^{60,67} Diffusion is evidently at the same rate across or parallel to fibrous structures, as for example in Mozzarella cheese.²⁹

Because diffusion of salt in cheese occurs simultaneously from several surfaces it is not easy to describe the process mathematically by applying solutions of Fick's second law. Simplified systems in which salt penetrates in one direction only from one surface have therefore been used to determine the diffusion coefficient from concentration curves: part of the cheese surface was covered with wax or other waterproof material,^{62,67} one flat surface of a model or a real cheese, or of plugs cut from unsalted cheese, was put in brine,⁶⁰ or salted and unsalted halves were pressed together, sometimes interlaid with filter paper.^{6,29,31,66}

In the present study a simple and miniaturised experimental procedure for diffusion measurements in cheese was developed, which was derived from the collaborative experiments on the diffusion of salt in agar gels.

Materials and Methods

Cheese

Sbrinz-type hard cheese was manufactured and treated in a pilot plant as in commercial practice.⁶⁸ Manufacturing was on a $\frac{1}{3}$ scale. The dimensions of the cheeses were approximately 35 cm diameter, 12–14 cm height and they weighed 12 kg. In order to obtain a uniform salt concentration gradient the curved side of the cheese was coated with petroleum jelly before brining. After pressing for 24 h the cheeses were immersed in a 20% brine bath for 4 days at 12°C.

Sampling

Two slabs differing in salt content were taken from the outer and central parts of the cheeses after brining, as illustrated in Fig. 3. The samples were analysed for water,⁶⁹ fat,⁷⁰ salt,⁷¹ pH and a_w (Ref. 54), and divided into

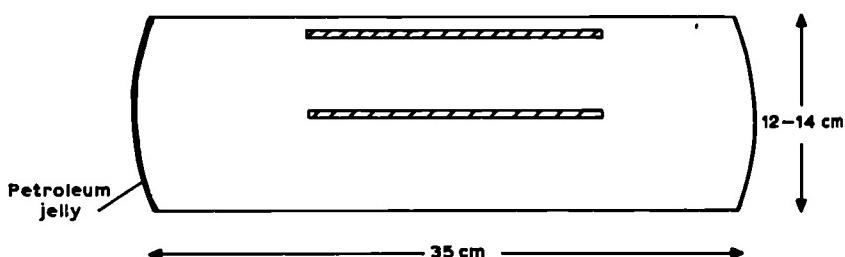


Fig. 3. Cross-section of cheese showing the sampling zones for diffusion experiments. (15 × 15 × 45 mm columns were cut out of the slices from the central and outer zone. The curved side was coated with petroleum jelly during brining.)

TABLE 6
COMPOSITION AND PROPERTIES OF THE SIX DAYS OLD CHEESE SAMPLES
(average values for the outer and central zone as illustrated in Fig. 3)

Cheese number	Zone	Water (% w/w)	Fat (% w/w)	Salt (% w/w)	pH	a_w
325	Outer	34.9	31.1	0.39	5.30	0.9844
	Middle	35.3	31.2	0.07	5.37	0.9850
326	Outer	35.9	30.1	0.52	5.25	0.9821
	Middle	36.4	30.3	0.07	5.24	0.9888
429	Outer	34.1	32.0	0.42	5.27	0.9870
	Middle	35.0	31.6	0.07	5.27	0.9930

15 × 15 × 45 mm columns. Cutting of the slabs and subsequent sample preparation was performed at 15°C to avoid exudation and consequent poor contact between the two columns. Table 6 shows the results of the chemical analyses.

Diffusion measurements

Columns from the central and outer zones were joined together. A small drop of distilled water was used to improve the contact at the junction. Under a stream of nitrogen, the pairs of columns were wrapped tightly in aluminium foil and fixed by means of gentle springs (approximately 0.5 N mm⁻¹) in plastic containers, as illustrated in Fig. 4. Sets of 4–6 pairs of columns were kept under nitrogen at 7, 11, 15 and 20°C in glass jars. After 5–7 days, the two halves were separated, weighed and cut into 12 slices. The slices were weighed, divided into small cubes (*ca.* 2 mm) and left for several hours in distilled water before analysing for chloride.⁷¹ The distance from the junction was calculated taking into account the weight of each slice.

Determination of the diffusion coefficient

The chloride concentrations in the slices were recalculated on a salt-in-moisture basis. Although the difference in water content between the two halves was small, the counterflow of water which occurred during equilibration was considered when recalculating the salt content of each slice. The change in water content in the regions of salt diffusion was assumed to be proportional to the change in salt concentration. The water content values in Table 6 were used and corrected with a factor which was proportional to the relative salt concentration difference. Salt-in-moisture values of the slices were plotted as a function of the distance from the

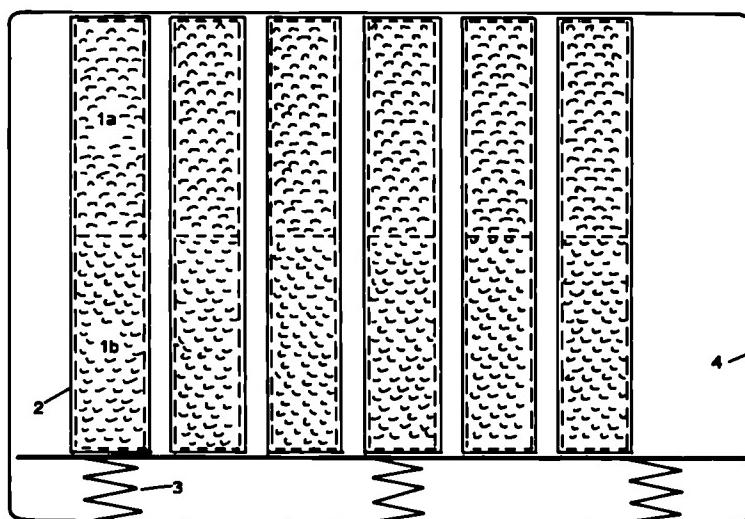


Fig. 4. Experimental procedure for diffusion measurements in cheese samples. (Pairs of columns of cheese with different salt contents (1a, 1b) are wrapped in aluminium foil (2) and fixed by means of gentle springs (3) in plastic containers (4). The containers are kept under nitrogen at constant temperature for several days, thus allowing uni-directional solute diffusion to take place under anaerobic conditions. (Glass jars for keeping the containers under nitrogen are not shown.)

junction, as shown in Fig. 5. The diffusion coefficient D_1 of salt in cheese moisture was then estimated from the concentration profiles according to the graphical method corresponding to eqn. (10).

Results and Discussion

The salt content of the cheese samples from the central part was in the range 0.20–0.23 g per 100 g moisture and typical for unsalted cheese curd. The salt concentrations in the columns from the outer part of the same cheese varied significantly, indicating a poor salt distribution in the horizontal slices. At the junction of the two columns the initial concentration gradient ranged from 0.2 to 1.4 g salt per 100 g cheese moisture.

Figure 5 shows typical salt concentration profiles observed after 5 days of diffusion at 15°C. At 7, 11 and 15°C, the sigmoid-shaped curves were almost symmetrical about the junction. The intercept of the curves with the junction line was on the average $\pm 0.04\%$ around the mean initial concentration. This small deviation was not statistically significant, indicating that the diffusion coefficient for the system tested was not

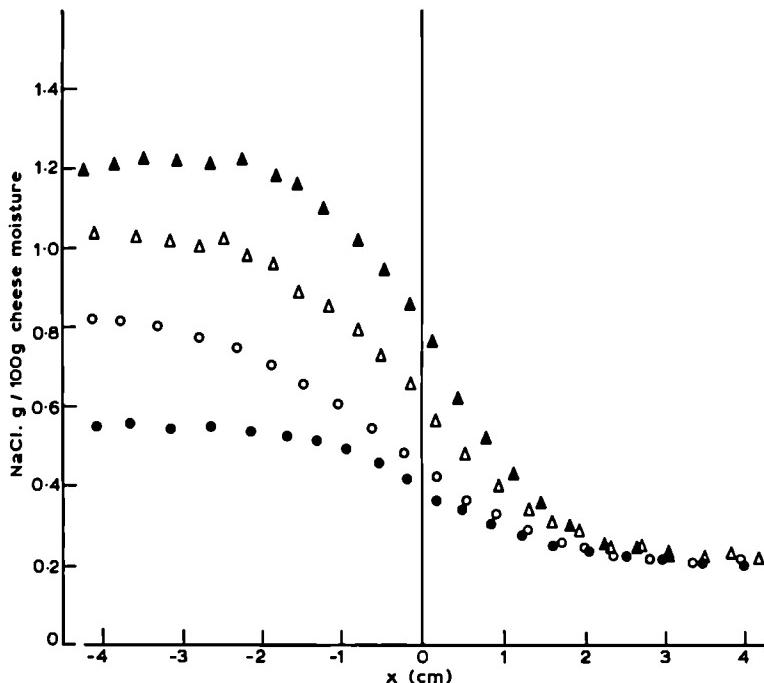


Fig. 5. Typical salt concentration profiles after 5 days of diffusion in cheese samples at 11°C. (Cheese numbers 325 (●, ○) and 326 (▲, △).)

concentration-dependent.¹⁴ At 20°C and after 120 h, however, the concentration-distance curves passed with one exception on the average 0·06% below the point corresponding to the mean initial concentration. It also appeared that the diffusion time of 120 h was too long for the length of the columns.

The apparent diffusion coefficients determined graphically from the experimental values near the junction as described in the experimental section are listed in Table 7 and the values are plotted against the reciprocal of temperature in Fig. 6. The D_t values ranged from $0\cdot81$ to $2\cdot18 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and the standard deviations for the determinations at constant temperature from $0\cdot15$ to $0\cdot27 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. The relative standard deviations ranged from 12 to 15%.

The D_t values in Table 7 are consistent with those reported by other authors for different cheese varieties. Extrapolating the data of Morris *et al.*⁶⁶ to a water content of 35% gives a D -value of about $1\cdot4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$

TABLE 7
**DIFFUSION COEFFICIENT FOR SALT IN CHEESE MOISTURE IN THE TEMPERATURE RANGE
 7–20°C**
 (Sbrinz-type hard cheese with 35% water and 31% fat (Table 6) expressed in g salt
 per 100 g cheese moisture)

Temp. (°C)	Cheese number	Diffusion time (h)	Salt concentration (% w/w)		D_t ($10^{-10} m^2 s^{-1}$)	s_D ($10^{-10} m^2 s^{-1}$)
			C_0	C_1		
7	325	120	0.19	0.58	1.15	
7	325	170	0.21	1.36	0.99	
7	325	170	0.21	0.80	0.81	
7	326	120	0.22	1.43	1.06	
7	326	170	0.23	1.10	1.22	
7	326	170	0.23	1.08	1.14	
Mean and standard deviation for 7°C values					1.06	0.15
11	325	120	0.21	1.00	1.24	
11	325	170	0.20	0.85	1.82	
11	325	170	0.22	0.98	1.38	
11	326	120	0.22	1.25	1.55	
11	326	170	0.23	1.16	1.33	
11	326	170	0.22	0.97	1.83	
11	429	118	0.21	0.44	1.53	
11	429	118	0.20	0.41	1.62	
11	429	118	0.20	0.46	1.59	
11	429	118	0.20	0.36	1.27	
11	429	118	0.20	0.50	1.25	
Mean and standard deviation for 11°C values					1.49	0.22
15	325	120	0.20	0.66	2.13	
15	325	170	0.21	0.81	1.50	
15	325	170	0.20	0.55	1.74	
15	326	120	0.23	1.40	1.79	
15	326	170	0.22	1.03	1.52	
15	326	170	0.22	1.22	1.57	
15	429	119	0.20	0.48	1.61	
15	429	119	0.20	0.45	1.67	
15	429	119	0.20	0.52	1.85	
Mean and standard deviation for 15°C values					1.71	0.20
20	429	120	0.20	0.61	1.70	
20	429	120	0.22	0.80	1.61	
20	429	120	0.22	0.85	2.18	
20	429	120	0.21	0.59	2.03	
Mean and standard deviation for 20°C values					1.88	0.27

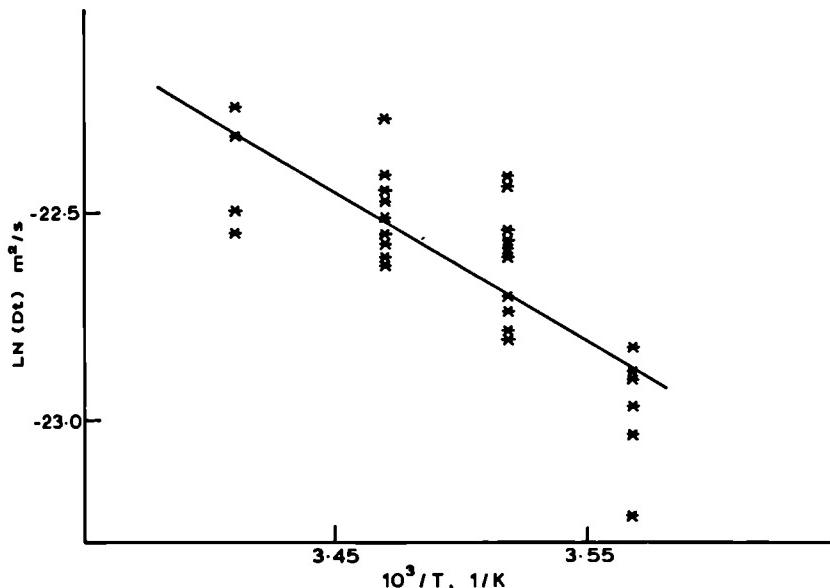


Fig. 6. Arrhenius plot for apparent diffusion coefficient of salt in cheese in the temperature range 7–20°C. (Sbrinz-type hard cheese with 35% water and 31% fat. The average initial salt concentration difference ranged from 0·2 to 1·2 g per 100 g cheese moisture.)

at 15–16°C. In the diagram published by Geurts *et al.*,⁶⁰ of D versus moisture content of cheese at 12·5°C, a value of about $1·1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ is obtained after extrapolation to 35% moisture content and 48% ratio of fat to non-fat solids.

Results in Table 7 also show that D_i increased with temperature from an average of 1·06 at 7°C to $1·88 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 20°C. From this increase a mean temperature coefficient of about $0·063 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \text{ }^\circ\text{C}^{-1}$ was calculated for the above-mentioned temperature range. Geurts *et al.*,⁶⁰ determined diffusion coefficients for salt in full-cream cheese with 43–44% water at 12·6, 18·0 and 20·1°C. From their data an average temperature coefficient of $0·12 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \text{ }^\circ\text{C}^{-1}$ is obtained. For comparison, the diffusion coefficient of salt in pure water increases from 10·6 at 12·6°C to $12·9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 20·1°C (Ref. 21). This corresponds to a temperature coefficient of $0·31 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \text{ }^\circ\text{C}^{-1}$.

Figure 6 shows the Arrhenius plot of $\ln D_i$ versus $1/T$. From the slope an activation energy of 29 kJ mol⁻¹ can be calculated. Without the data at 7°C, which lie somewhat below the regression line in Fig. 6, a value of 18 kJ

mol^{-1} is obtained. This value may be compared to that found for salt in agar gels (Table 5).

CONCLUSIONS

The collaborative study of uni-directional salt diffusion in agar gels has shown that the diffusivity of solutes in model foods can be obtained with reasonable accuracy using the technique of semi-infinite cylinders, together with the appropriate diffusion equation. The type of method used for calculation of the diffusivity from the concentration-distance curves affects to some extent the resulting coefficient. A non-linear regression procedure is recommended and that account is taken of the results from the whole length of the cylinders. The experimental error in the participating laboratories was on the average below 10%. The relatively low reproducibility of the measurements between the laboratories indicates that the experimental procedure was not sufficiently uniform. A more uniform preparation of the gels and determination of the solute concentration after diffusion would probably improve the reproducibility.

From the results on cheese, it may be concluded that the experimental technique tested is suitable for studying salt diffusion in this product. Using relatively small cheese samples, multiple data can be collected within a few days. Using the simple graphical method (eqn. (11), tangent drawn by eye at the inflection point of the concentration-distance curves), the apparent diffusion coefficient can be estimated with a relative standard deviation of about 14%. The technique could be adapted for investigations of other diffusing solutes and other foods.

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APPENDIX: TYPICAL RAW DATA OBTAINED FROM THE LABORATORIES AND USED FOR THE PLOTS IN FIG. 1

The data used correspond to the experiment GR 02 1/0 with the following operating conditions:

$$T = 25^\circ\text{C} \quad C_0 = 0.144\% \text{ w/w} \quad C_1 = 1.440\% \text{ w/w}$$

Agar concentration = 3.0% w/w Diffusion time = 6.00 h

<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)	<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)
1	-18.400	1.44	13	2.600	0.70
2	-16.600	1.43	14	4.400	0.54
3	-14.900	1.42	15	6.100	0.44
4	-13.100	1.42	16	7.900	0.37
5	-11.400	1.37	17	9.600	0.28
6	-9.600	1.29	18	11.400	0.23
7	-7.900	1.23	19	13.100	0.26
8	-6.100	1.14	20	14.900	0.20
9	-4.400	1.06	21	16.600	0.17
10	-2.600	1.00	22	18.400	0.18
11	-0.900	0.98	23	20.100	0.14
12	0.900	0.64			

One coefficient identification:

$$\text{Crit} = 4.023E - 002 \quad \text{MSD} = 8.916E - 003 \quad D = 1.451E - 009 \text{ m}^2 \text{ s}^{-1}$$

Three coefficient identification:

$$\begin{aligned} \text{Crit} &= 3.506E - 002 & \text{MSD} &= 8.730E - 003 \\ C_0 &= 0.150\% \text{ w/w} & C_1 &= 1.464\% \text{ w/w} & D &= 1.525E - 009 \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

The data used correspond to the experiment RU 03 1/0 with the following operating conditions:

$$T = 25^\circ\text{C} \quad C_0 = 0.000\% \text{ w/w} \quad C_1 = 1.073\% \text{ w/w}$$

Agar concentration = 3.0% w/w Diffusion time = 14.00 h

<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)	<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)
1	-42.970	1.08	12	-1.410	0.58
2	-37.940	1.08	13	1.440	0.47
3	-32.820	1.06	14	4.350	0.42
4	-28.630	1.07	15	7.430	0.28
5	-24.990	1.05	16	10.820	0.19
6	-21.140	1.04	17	14.530	0.12
7	-17.300	1.00	18	18.410	0.06
8	-13.670	0.94	19	22.670	0.03
9	-10.340	0.86	20	27.220	0.01
10	-7.240	0.77	21	31.830	0.00
11	-4.310	0.68			

One coefficient identification:

$$\text{Crit} = 2.272E - 003 \quad \text{MSD} = 2.326E - 003 \quad D = 1.425E - 009 \text{ m}^2 \text{ s}^{-1}$$

Three coefficient identification:

$$\begin{aligned} \text{Crit} &= 2.107E - 003 & \text{MSD} &= 2.361E - 003 \\ C_0 &= -0.006\% \text{ w/w} & C_1 &= 1.077\% \text{ w/w} & D &= 1.477E - 009 \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

The data used correspond to the experiment PA 03 1/0 with the following operating conditions:

$$T = 25^\circ\text{C} \quad C_0 = 0.010\% \text{ w/w} \quad C_1 = 1.040\% \text{ w/w}$$

Agar concentration = 3.0% w/w Diffusion time = 6.00 h

<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)	<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)
1	-10.400	1.04	9	1.000	0.48
2	-9.100	0.93	10	2.300	0.38
3	-7.700	0.91	11	3.700	0.36
4	-6.300	0.78	12	5.000	0.25
5	-4.800	0.78	13	6.400	0.22
6	-3.700	0.69	14	7.600	0.14
7	-2.500	0.62	15	8.700	0.08
8	-1.200	0.57			

One coefficient identification:

$$\text{Crit} = 1.890E - 002 \quad \text{MSD} = 9.487E - 003 \quad D = 1.205E - 009 \text{ m}^2 \text{ s}^{-1}$$

Three coefficient identification:

$$\begin{aligned} \text{Crit} &= 1.147E - 002 & \text{MSD} &= 7.983E - 003 \\ C_0 &= -0.257\% \text{ w/w} & C_1 &= 1.283\% \text{ w/w} & D &= 2.919E - 009 \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

The data used correspond to the experiment GD01 1/03 with the following operating conditions:

$$T = 25^\circ\text{C} \quad C_0 = 0.070\% \text{ w/w} \quad C_1 = 1.000\% \text{ w/w}$$

Agar concentration = 3.0% w/w Diffusion time = 6.00 h

<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)	<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)
1	-18.860	1.00	13	0.490	0.52
2	-17.210	0.99	14	1.840	0.46
3	-15.640	0.99	15	3.460	0.34
4	-14.060	0.96	16	4.990	0.29
5	-12.480	0.95	17	6.510	0.23
6	-10.970	0.93	18	8.030	0.18
7	-9.400	0.91	19	9.700	0.14
8	-7.420	0.87	20	11.390	0.11
9	-5.500	0.78	21	12.950	0.09
10	-3.940	0.73	22	14.560	0.07
11	-2.430	0.67	23	17.850	0.06
12	-0.870	0.59	24	16.220	0.07

One coefficient identification:

$$\text{Crit} = 3.302E - 003 \quad \text{MSD} = 2.446E - 003 \quad D = 1.134E - 009 \text{ m}^2 \text{ s}^{-1}$$

Three coefficient identification:

$$\begin{aligned} \text{Crit} &= 2.590E - 003 & \text{MSD} &= 2.267E - 003 \\ C_0 &= 0.060\% \text{ w/w} & C_1 &= 1.000\% \text{ w/w} & D &= 1.182E - 009 \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

The data used correspond to the experiment CH06 1/03 with the following operating conditions:

$$T = 25^\circ\text{C} \quad C_0 = 0.024\% \text{ w/w} \quad C_1 = 1.030\% \text{ w/w}$$

Agar concentration = 3.0% w/w Diffusion time = 6.00 h

<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)	<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)
1	-19.280	1.03	13	2.350	0.40
2	-17.700	1.01	14	3.980	0.34
3	-16.100	1.04	15	5.620	0.26
4	-14.510	0.99	16	7.270	0.22
5	-12.820	0.97	17	8.980	0.16
6	-11.080	0.93	18	10.700	0.12
7	-9.290	0.89	19	12.320	0.09
8	-7.500	0.87	20	14.000	0.07
9	-5.740	0.77	21	15.670	0.05
10	-4.020	0.71	22	17.380	0.04
11	-0.800	0.61	23	19.200	0.03
12	0.780	0.48			

One coefficient identification:

$$\text{Crit} = 5.346E - 003 \quad \text{MSD} = 3.250E - 003 \quad D = 1.543E - 009 \text{ m}^2 \text{ s}^{-1}$$

Three coefficient identification:

$$\begin{aligned} \text{Crit} &= 5.294E - 003 & \text{MSD} &= 3.392E - 003 \\ C_0 &= 0.020\% \text{ w/w} & C_1 &= 1.034\% \text{ w/w} & D &= 1.591E - 009 \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

The data used correspond to the experiment ST 13 1/0 2 with the following operating conditions:

$$\begin{array}{lll} T = 25^\circ\text{C} & C_0 = 0.010\% \text{ w/w} & C_1 = 0.300\% \text{ w/w} \\ \text{Agar concentration} = 2.0\% \text{ w/w} & & \text{Diffusion time} = 6.00 \text{ h} \end{array}$$

<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)	<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)
1	-22.240	0.30	8	1.770	0.12
2	-18.840	0.30	9	5.240	0.08
3	-15.570	0.29	10	8.660	0.05
4	-12.290	0.29	11	12.010	0.03
5	-8.850	0.26	12	15.310	0.02
6	-5.220	0.23	13	18.750	0.01
7	-1.690	0.17	14	22.190	0.01

One coefficient identification:

$$\text{Crit} = 2.824E - 004 \quad \text{MSD} = 1.246E - 003 \quad D = 1.390E - 009 \text{ m}^2 \text{ s}^{-1}$$

Three coefficient identification:

$$\begin{array}{lll} \text{Crit} = 2.718E - 004 & \text{MSD} = 1.328E - 003 \\ C_0 = 0.009\% \text{ w/w} & C_1 = 0.300\% \text{ w/w} & D = 1.405E - 009 \text{ m}^2 \text{ s}^{-1} \end{array}$$

The data used correspond to the experiment HA 02 1/0 with the following operating conditions:

$$\begin{array}{lll} T = 25^\circ\text{C} & C_0 = 0.020\% \text{ w/w} & C_1 = 1.100\% \text{ w/w} \\ \text{Agar concentration} = 3.0\% \text{ w/w} & & \text{Diffusion time} = 6.00 \text{ h} \end{array}$$

<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)	<i>N</i>	<i>X</i> (mm)	<i>C</i> (% w/w)
1	-17.100	1.10	13	0.700	0.46
2	-15.650	1.02	14	2.050	0.41
3	-14.150	1.04	15	3.850	0.34
4	-12.500	0.99	16	5.600	0.26
5	-11.100	0.94	17	6.800	0.23
6	-9.600	0.93	18	8.250	0.19
7	-7.950	0.82	19	9.750	0.12
8	-6.750	0.85	20	11.200	0.10
9	-5.500	0.79	21	13.000	0.08
10	-3.950	0.74	22	14.600	0.06
11	-2.650	0.76	23	15.600	0.03
12	-0.950	0.62	24	16.800	0.02

One coefficient identification:

$$\text{Crit} = 3.452E - 002 \quad \text{MSD} = 7.909E - 003 \quad D = 1.714E - 009 \text{ m}^2 \text{ s}^{-1}$$

Three coefficient identification:

$$\begin{array}{lll} \text{Crit} = 2.179E - 002 & \text{MSD} = 6.575E - 003 \\ C_0 = -0.004\% \text{ w/w} & C_1 = 1.078\% \text{ w/w} & D = 1.722E - 009 \text{ m}^2 \text{ s}^{-1} \end{array}$$

8

Diffusivity of Volatiles in Water in the Presence of a Third Substance

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SUMMARY

The diffusion of aromatic compounds at low concentrations in water is affected by the presence of a second solute. This problem is of paramount importance in the food industry because it is the key to aroma retention. This chapter presents experimental values for small molecule diffusion coefficients at various concentrations of the second solute. The technique of analysing concentration profiles in gelled solutions has been widely used within the COST 90bis project.

NOMENCLATURE

a_w	water activity
D_a	diffusivity of volatile ($\text{m}^2 \text{s}^{-1}$)
D_{a0}	diffusivity of volatile in pure water
l	distance between a point and the source (m)
R	universal gas constant
t	time (s)
T	temperature (K)
T_0	temperature at which D_{a0} is measured

T_A	constant
x_w	molar fraction of water
W_a	mass fraction of volatile
W_{a0}	initial mass fraction of volatile
W_s	mass fraction of substrate
η	coefficient of dynamic viscosity (mPa s)
η_0	coefficient of dynamic viscosity of pure water
α	constant

INTRODUCTION

For diffusivities in binary liquid systems, a vast quantity of data can be found in the literature (Johnson and Babb, 1956; Ghai *et al.*, 1973; Erth *et al.*, 1974; Reid *et al.*, 1977). Three techniques were generally used: concentration profile, capillary cell and Stokes' methods. The most usual system is the porous diaphragm cell which consists of two liquid phases, one containing the diffusing substance, separated by a porous membrane; this technique was first used by Stokes (1950) to study the diffusion of potassium chloride in water at 25°C. The capillary cell method was used by Wang (1951) to study self-diffusion of water. For the concentration profile method, a gelling agent was employed to give 'structure' to the medium; in 1930 Friedman and Kraemer studied the diffusion of a solute from a gel towards water and conversely; the substrates were urea, sucrose, glycerine or lactose. Belton and Wilson (1982) and Naesens *et al.* (1981) used two columns of gel. In this work, this last technique was employed to study the behaviour of small molecules in ternary systems over a wide range of concentrations under various conditions. Data for ternary systems is much more sparse than that for binary systems, especially for aqueous solutions of macromolecules.

MATERIALS AND METHOD

The model systems used were concentrated solutions of non-volatile compounds (the second solutes or substrates) and various volatile compounds in very dilute concentrations.

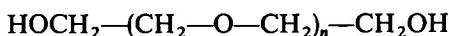
Polyethylene glycols (PEGs) and sugars were chosen as substrates because they provided a wide range of molecular weights. PEGs are employed in the chemical and related industries, and have the advantage of being more

TABLE 1
CHARACTERISTICS OF SOME OF THE SUBSTRATES (25°C)

	Sugars			PEGs	
	MD 63 (DE 61.5)	MD 33 (DE 31)	MD 05 (DE 20)	600	1500
Mean molecular weight	291	560	868	600	1 500
Solubility in water (W_s %)	90	80	70	—	75
At the same mass fraction in water, $W_s = 50\%$					
Density	1.2354	1.2423	1.2443	1.0852	1.0869
Water activity	0.933	0.956	0.969	0.908	0.919
Viscosity (mPa s)	14.0	42.7	113.5	18.6	39.4

uniform in molecular weight than polysaccharides. Mono-, oligo- and polysaccharides are widely used in the food industry itself. These two types of substrate have the same alcohol chemical function but different structural details.

The PEGs are synthetic polymers of the general formula



and have the same basic component: ethylene glycol (molecular weight = 62).

In the case of sugars, six compounds were employed: dextrose, maltose, maltotriose and three spray-dried liquid glucose syrups (prepared from hydrolysed corn starch), the basic unit of which is glucose. The individual glucose syrups are characterised by their dextrose equivalent (DE), which represents the weight of reducing sugars (g) per 100 g dry matter as equivalent dextrose. The mean molecular weights of glucose syrups are obtained by cryometry, and for PEGs the values were provided by the manufacturers and confirmed at ENSBANA (Dijon).

All these substrates can be dissolved in water and Table 1 shows the differences in behaviour:

- at the same molecular weight, glucose syrups are less soluble than PEGs but more soluble than pure sugars; and
- at the same mass fraction, the density, water activity (a_w) and viscosity (η) of sugar solutions are all greater than for PEGs; all the solutions are Newtonian.

TABLE 2
CHARACTERISTICS OF THE VOLATILES

Volatile	Acetone	Ethyl acetate	2-Propanol	<i>n</i> -Hexanol	Diacetyl
Molecular weight	58.68	88.10	60.09	102.17	86.09
Density (at 20°C)	0.792	0.901	0.785	0.818	0.990
Solubility in water (g/100 ml).	Very soluble	8.6 (20°C)	Very soluble	5.9 (20°C)	250 (15°C)
Boiling point (°C)	56.5	77.15	82.3	157.2	88
Molar volume	74.0	106.0	81.5	148	96

The volatiles are given in Table 2. They represent different chemical functions and are very common in aromatic food products. They were used at very low concentrations (below 0.1%) in the aqueous solutions.

The measurement of volatile diffusivity was performed by the concentration profile technique described by Voilley and Bettenfeld (1985). The procedure was the same for sugar and PEG solutions, except for the gelling agent: agar-agar in the case of sugars and polyacrylamide gel in the case of PEG. The diffusivity of the volatiles was calculated using the well-

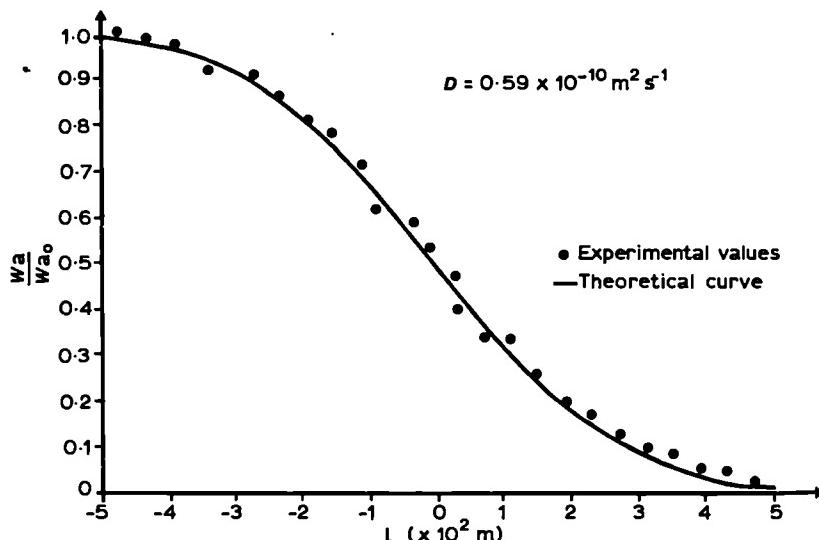


Fig. 1. Concentration profile of diacetyl in a 50% MD 33 gelled solution (25°C)

TABLE 3
DIFFUSIVITY ($D (10^{-10} \text{ m}^2 \text{ s}^{-1})$) IN GEL (AGAR-AGAR 1%) OF VOLATILES COMPARED TO
VALUES IN WATER

Temperature (°C)	Acetone	Ethyl acetate	2-Propanol	Reference
25	—	—	11·4	Brown and Chitumbo (1975)
	12·8	—	10·8	Hayduk and Laudie (1974)
	15·6	—	11·4	Johnson and Babb (1956)
	—	11·8	—	Frey and King (1982)
	12·7	11·7	10·2	This work
35	—	16·6	—	Chandrasekaran and King (1972)
	16·9	14·8	13·8	This work
45	—	18·3	—	Frey and King (1982)
	22·0	18·3	16·9	This work

known solution of Fick's second law given by Crank (1975) for a semi-infinite body:

$$\frac{W_{a(l,t)}}{W_{a0}} = \frac{1}{2} \operatorname{erfc} \frac{l}{2\sqrt{D_a t}}$$

This method has been extensively used during the COST 90bis project. Numerical difficulties have been analysed by Gros and Rüegg (Chapter 7). The underlying assumptions for the use of the above solution are that neither the water flux nor the second solute flux are significant, which is reasonable since the volatile concentrations are very small and the fluxes of the substrates would only be those due to counter-diffusion as the volatiles are moving. So there is no necessity to introduce cross-terms in the volatile flux equation. An example of experimental results is given in Fig. 1.

The repeatability, expressed by the variation coefficient, is better than 10%. Belton and Wilson (1982) indicated a repeatability of about 10% for a rather similar method. The gelling agent has no effect on the diffusivity, as is confirmed by the comparison of values obtained by other techniques, in pure water (Table 3).

RESULTS AND DISCUSSION

Nature and Concentration of Volatiles

The diffusivity of volatiles at low concentration in water (at 25°C) depends slightly on their nature. For the two pure compounds (acetone and *n*-hexanol) with the most different combinations of molar volumes, molecular

TABLE 4
DIFFUSIVITY OF VOLATILES AT INFINITE
DILUTION IN WATER
(25°C) (D ($10^{-10} \text{ m}^2 \text{ s}^{-1}$)))

Acetone	12.7
Ethyl acetate	11.7
2-Propanol	10.2
Diacetyl	8.5
<i>n</i> -Hexanol	5.6

weights and boiling points, the diffusivity varies by a factor of two (Table 4).

The initial concentration of the volatile, for example acetone (Table 5), affects moderately the value of diffusivity over the range of mass fractions 0.6–13.7%. Some authors report larger variations in diffusivity at higher concentrations. Reid and Sherwood (1966) noted an increase and then a decrease in diffusivity over the whole range of acetone mole fraction.

Nature and Concentration of Substrates

The diffusivities of three volatiles are shown in Fig. 2 as a function of the mean molecular weight of sugars present. Diffusivity is not significantly affected by this variable. Chandrasekaran and King (1972) also observed no change in diffusivity for ethyl acetate in aqueous solutions of glucose, fructose and sucrose.

The diffusivity of acetone is slightly greater when PEGs are used as substrates as compared with sugars (Table 6).

A marked decrease in the diffusivity of all volatiles is observed when the

TABLE 5
DIFFUSIVITY OF ACETONE IN 50% GLUCOSE SOLUTIONS (25°C)

Acetone mass fraction (W_s %)	Diffusion time (h)	Diffusion coefficient ($10^{-10} \text{ m}^2 \text{ s}^{-1}$)
0.6	138	1.21
3.4	118	1.28
4.0	118	1.57
6.4	139.5	1.46
6.4	139.5	1.65
12.7	143.5	1.59
13.7	143.5	1.73

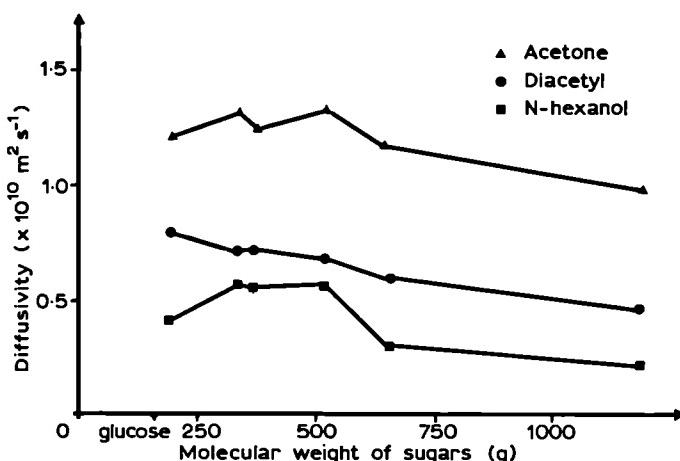


Fig. 2. Diffusivity of volatiles as a function of molecular weight of sugars.

substrate solute mass fraction is increased (Fig. 3). Similar results were obtained by Furuta *et al.* (1984) for ethanol in aqueous solutions of maltodextrin.

The diffusivity of the three volatiles shows a ten-fold decrease over a glucose syrup concentration change from 0 to 50% and this decrease is much greater for *n*-hexanol ($\times 28$) than for acetone ($\times 12$) between 50 and 70% sugar concentrations. The same type of results is obtained in the presence of PEG 600 (Table 7).

TABLE 6
DIFFUSIVITY OF ACETONE IN
50% SUBSTRATE SOLUTIONS (25°C)
($D (10^{-10} \text{ m}^2 \text{s}^{-1})$)

Water	12.70
Glucose	1.21
Maltose	1.25
MD 63	1.32
MD 05	0.97
PEG 600	1.81
PEG 1500	1.37

Effect of Temperature

As would be expected, the diffusivity of volatiles increases with temperature (Fig. 4). The activation energy for diffusion calculated according to the

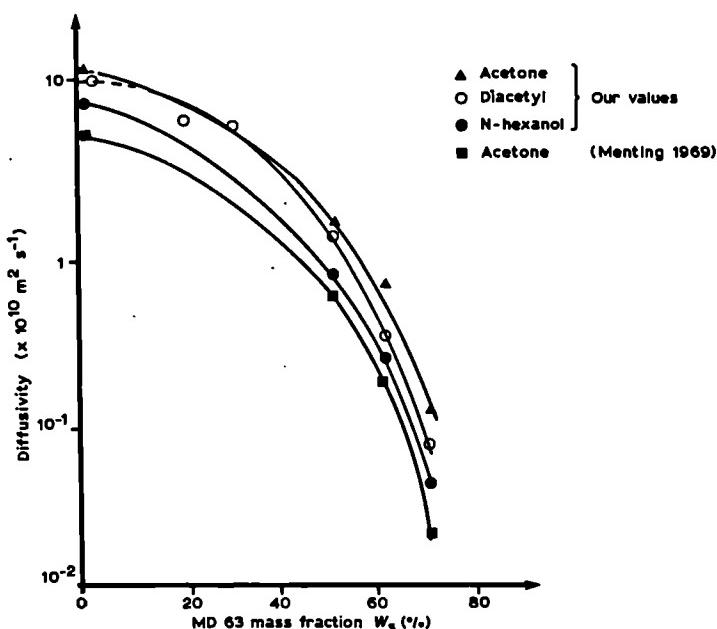


Fig. 3. Diffusivity of volatiles as a function of sugar concentration.

TABLE 7
DIFFUSIVITY OF ACETONE IN TWO SUBSTRATE
SOLUTIONS OF VARYING CONCENTRATION (25°C)

	<i>Mass fraction</i> (W_s %)	<i>D</i> ($10^{-10} m^2 s^{-1}$)
Water	—	12.7
Glucose	15	—
	50	1.21
PEG 600	30	2.55
	50	1.81
	70	0.85
	85	—

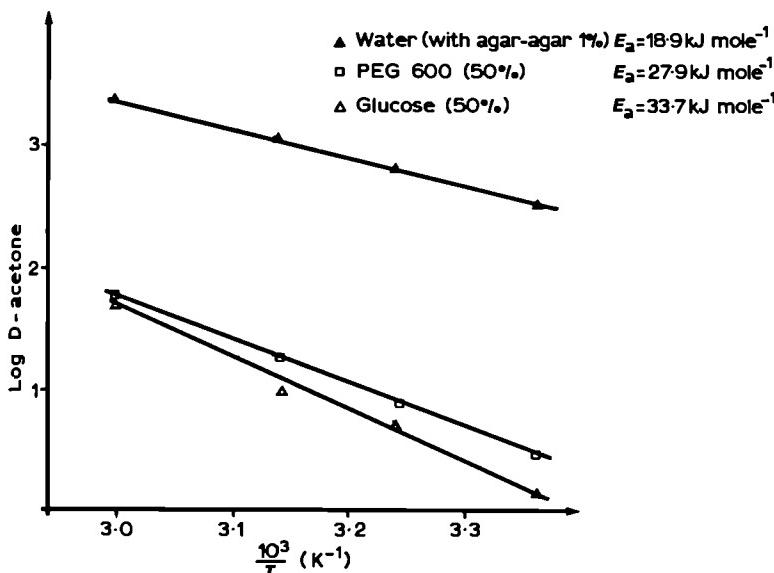


Fig. 4. Diffusivity of acetone as a function of temperature.

Arrhenius law shows significant differences depending on whether the volatile compound is in water or in the presence of substrates. The degree of interaction of acetone in the substrate solutions can be deduced to be greater than it is in water.

Water Activity and Viscosity of the Solutions

Water activity varies with mass fraction and the nature of the substrates. Only the first of these two factors affects the diffusivity noticeably. The diffusivity of volatiles is inversely proportional to the 0.87 power of the dynamic viscosity of the solutions (Fig. 5).

As an example, the correlation coefficient is 0.97 for *n*-hexanol. The index is not very different from 1 for all these volatiles. This fact indicates that the size of the diffusing molecules is not a significant factor because the molecules of all the volatiles are large compared to those of the substrate.

These separate observations lead one to conclude that the most important factor is the water mass fraction or the substrate mass fraction. In order to include this factor in a general correlation representing all the measured diffusivities for a given volatile–substrate pair, use can be made of the viscosity of the solution. Viscosity is generally related to the density and

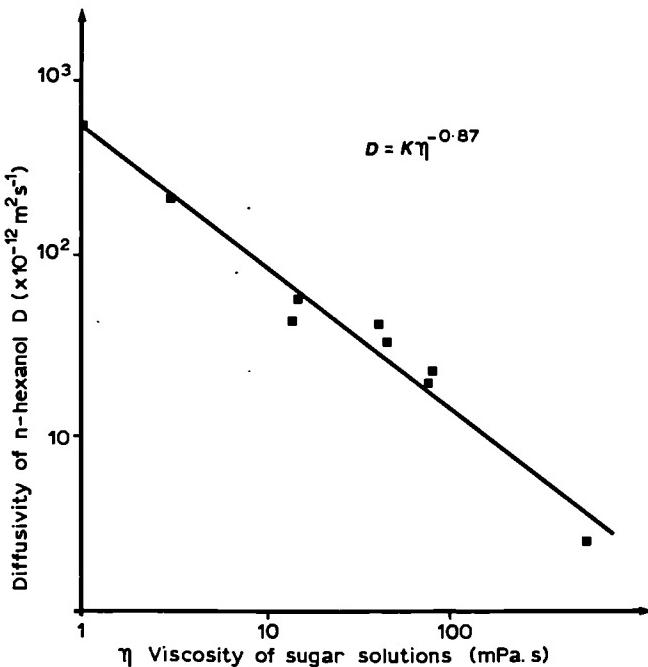


Fig. 5. Diffusivity of a volatile as a function of the viscosity of the sugar solutions.

therefore includes indirectly the substrate mass fraction (Reid *et al.*, 1977). So the following correlation is proposed:

$$D_a = D_{a0} x_w \left(\frac{\eta_0}{\eta} \right)^\alpha \exp \left[T_A \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]$$

where D_{a0} is the diffusivity of volatiles in pure water at T_0 , as given in Table 4; x_w is the water molar fraction; and η_0 and η are the viscosities of pure water at T_0 and of the medium at T .

The constants α and T_A are specific to one volatile–substrate system, although (except for acetone pairs) they do not show great variations (Table 8). The energy RT_A is only a part of the activation energy of diffusion since the variation of η is also temperature-dependent. The water molar fraction indicates the role played by water activity: this term remains close to unity and therefore could easily be omitted to produce an even simpler correlation.

TABLE 8
CONSTANTS IN THE CORRELATION

Component pair	α	T_A
Acetone-sugar	0.82	814
Acetone-PEG	0.59	572
Ethyl acetate-sugar	0.88	162
Ethyl acetate-PEG	0.49	6539
2-Propanol-sugar	0.74	754
Diacetyl-sugar	0.94	956
n-Hexanol-sugar	1.06	1230

CONCLUSION

The method using concentration profiles in gelled solutions is applicable to the measurement of the diffusivity of volatiles in aqueous solutions of various substrates. The diffusivity of such volatiles at very low concentration depends very much on the water mass fraction. This variable can be incorporated in a general correlation of diffusivity with the viscosity of the solution.

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DISCUSSION

R. Jowitt sought clarification from *J. B. Gros* of his penultimate recommendation that 'the maximum plateaux regions should be ensured'. Surely the maximum plateaux were those at the start of the experiment? *Gros* explained that the plateaux at the *end* of the experiment should always be substantial for best results. This was not always the case with the results from some participants. *D. Ehlermann* proposed two reasons why this was important: first, to ensure that throughout the 'source' and 'sink' conditions, C_1 and C_0 , were always present to maintain the conditions of the experiment; and second, to ensure that the mathematical conditions required by the model to enable it to represent correctly the physical conditions were always present. For the former a long cylinder might be advisable; for the latter it was enough for C_1 and C_0 to remain the same until the end of the experiment.

W. E. L. Spiess took the opportunity presented by the papers on salt diffusion in agar models and cheese to refer again to the justification for using the glass microsphere model system described earlier. Participants were not really interested in diffusion in agar gels or in beds of glass spheres; they were much more interested in practical aspects concerning real foods.

However, in order to provide a secure basis for collaborative—or indeed individual work—on complex, variable, actual foods, the Project had sought earnestly for suitable systems and substances which could be relied on for their consistency and stability for preparatory and ‘calibration’ purposes. The gel and microsphere work was, he felt, quite justified. Unfortunately, the Project was not long enough to enable participants always to proceed from the models to the actual foods. Projects should be much longer. Happily, in the case of salt diffusion, valuable results had been obtained with cheese as well as with gel, providing vindication within the space of the Project time span on this occasion.

E. U. Schlünder remarked on the high value ($\simeq 10^{-10} \text{ m}^2 \text{ s}^{-1}$) of the diffusivity of salt in cheese, which was closer to the values commonly associated with diffusion in liquids. Was this diffusion in a solid or in a liquid—or diffusion at all?! *M. Rüegg* explained that although ostensibly a solid, cheese contained sufficient water ($\simeq 30\%$) for salt diffusion to take place in the aqueous phase of the cheese and to be described by a single diffusion coefficient. *Schlünder* then commented that diffusivities in sugar solutions reported by Voilley and Roques were around 10^{-11} or 10^{-12} , which were orders of magnitude less than those for the salt in the cheese. *Rüegg* agreed and suggested that this might be due to the considerably greater viscosity of the sugar solutions in question than that of the aqueous phase in cheese. It was quite an interesting comparison which *Schlünder* had pointed out.

Diffusion of Sodium Chloride in Green Olives

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INTRODUCTION

Large quantities of olives are processed and stored in brines containing various amounts of sodium chloride. The salt acts as a preservative, controlling desirable lactic acid fermentation. Storage of green olives in brines for several days or months can remove, by leaching, the bitter component oleuropein, a glucoside which can also be hydrolysed with alkali (Shasha and Leibowitz, 1959).

In the production of Spanish-type olives, the bitter component is hydrolysed by pretreatment of the green olives in a solution of 1·8% sodium hydroxide for a few hours. The olives are then stored in a brine containing about 10% sodium chloride, when lactic acid fermentation takes place for several days (Samish, 1955).

Diffusion of salt plays an important role in the processing and storage of olives. However, no quantitative data on the diffusivity of salt in olives are available in the literature. By contrast, the diffusion of salt in pickles, in connection with the brining and desalting of cucumbers, has been studied thoroughly (Pflug *et al.*, 1967). The purpose of this investigation was to estimate the diffusivity of sodium chloride in green olives from controlled diffusion experiments and to evaluate the effect of alkali pretreatment on salt diffusion.

EXPERIMENTAL PROCEDURE

Experimental measurements of salt diffusion in green olives of the 'Konservolia' variety, grown in Central Greece, were made during the 1985-86 season. The olives were picked at commercial maturity and sorted to a uniform large size of mean count 143 olives per kg. The olives had an ellipsoid shape with dimensions $d_1 = 2.05-2.14$ cm and $d_2 = 2.7-2.8$ cm. The weight of the pit was about 13% of the weight of the whole olive.

Diffusion of sodium chloride in olives was studied in several 1-litre glass jars containing brines of five salt concentrations (7.6-16.2%). A known number of olives (30) were weighed and placed in each jar, which was closed and stored at room temperature (18°C). The jars were shaken daily to ensure uniform brine concentration. Samples of 0.5 ml brine were taken from each jar at fixed time intervals and titrated with silver nitrate for sodium chloride. The amount of salt taken up by the olives was calculated from the difference in brine concentration.

Sample No. 5 contained olives pretreated with alkali to hydrolyse oleuropein. The olives were immersed in a solution of 1.8% sodium hydroxide at room temperature for 6 h, rinsed with water three times and kept in clear water for 2 days to remove the alkali residues.

ESTIMATION OF DIFFUSIVITY

The fractional salt uptake (absorption) was expressed as the ratio M_t/M_∞ , where M_t is the salt uptake after time t in the brine and M_∞ is the equilibrium salt uptake, which was reached within 50 days. Plots of M_t/M_∞ versus time (t) showed an increased rate of salt uptake as the mean brine concentration was increased from 7.2 to 15.3% NaCl. The uptake was much faster in olives pretreated with alkali.

The experimental system used in this work corresponds to diffusion in spheres from a stirred solution of limited volume (Crank, 1975). A similar system has been used for the estimation of salt diffusivity in pickles (Pflug *et al.*, 1967). The olives were assumed to be spherical with an equivalent radius $R = 1.22$ cm. The unsteady state diffusion equation for spheres was used, assuming radial diffusion into isotropic spheres (same diffusivity of salt in the flesh and the pits of the olives). The initial salt concentration in the olives was assumed to be zero ($C_0 = 0$). In addition, the following boundary conditions were assumed: at $r = 0$, $\partial C/\partial r = 0$; at $r = R$, $V(\partial C/\partial r) = D(\partial C/\partial r)$,

where C is the salt concentration, V is the volume of the brine and R is the radius of the olive. As a simplification, it was assumed that the salt concentration in the solution was equal to the salt concentration in the surface layer of the olives.

The solution of the diffusion equation for this system is given by Crank (1975) as a diagram of (M_t/M_∞) versus $(Dt/R^2)^{1/2}$ for various equilibrium salt uptakes ($\% M_\infty/VC_0$). The mean diffusivity (D) was estimated from the experimental half-equilibrium time (at $M_t/M_\infty = 0.5$) using a constant radius R for the olives, since no appreciable shrinkage was detected. The estimated values of the diffusivity of salt in green olives are shown in Table 1.

TABLE 1
DIFFUSIVITY OF SODIUM CHLORIDE IN GREEN OLIVES
(18°C)

<i>Sample</i>	<i>Mean brine concentration</i> (% NaCl)	<i>Diffusivity of sodium chloride</i> ($D \times 10^{12} \text{ m}^2 \text{ s}^{-1}$)
1	7.2	3.2
2	9.8	5.0
3	11.7	5.7
4	15.3	7.9
5 (pretreated with 1.8% sodium hydroxide)	10.7	14.81

The diffusivity of salt in the green olives increased fairly linearly from 3.2×10^{-12} to $14.8 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ as the mean brine concentration was increased from 7.2 to 15.3% NaCl. The estimated diffusivities of salt in olives are about two orders of magnitude smaller than the diffusivity of salt in pickles, found to be about $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ by Pflug *et al.* (1967).

The salt diffusivity increased considerably (almost threefold) in olives pretreated with alkali. This significant increase in the diffusion rate is an added advantage of the alkali pretreatment process.

The relatively low diffusivity of sodium chloride in olives may be caused by the resistance to mass transfer of the skin and the compact flesh of the olives. The olives contain a large percentage of oil, which is known to retard the diffusion of various oil-insoluble molecules and ions.

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Diffusion of Sodium Chloride into Agarose Gel

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EDITOR'S NOTE

This contribution did not constitute a paper or poster at the seminar but was felt to be sufficiently relevant to warrant its inclusion in these Proceedings. Readers should bear in mind the original date of this contribution in relation to others in this publication.

EXPERIMENTAL

The experiments below were carried out as a third year undergraduate research exercise in 1985 as a contribution to the COST 90bis cooperative programme.

Firm agarose gels (3 wt%) were prepared by heating the agarose powder (BDH) and water mixture up to 100°C for 20 min and then pouring the hot solution into glass cylinders 10 cm long and 18 mm in diameter. The gel tube was connected to a salt solution reservoir containing 0.02 M (0.117 wt%) NaCl by a Sovirel O-ring seal and screw cap. The system was closed and immersed horizontally in a water bath at 25°C. After each run, the gel was sliced into discs and analysed for chloride ion by potentiometric titrations. A correction was made for a small amount of chloride in the gel itself. It proved helpful to break up the gel discs both mechanically and then with an ultrasonic probe.

The diffusion coefficients D in the gel were calculated by means of eqn. (1):

$$\frac{c}{c_0} = \frac{1}{2} \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right) \quad (\text{Ref. 1}) \quad (1)$$

where c was the salt concentration at a distance x from the interface at time t and c_0 was the initial salt concentration. The resulting D values increased with distance from the interface. This showed that the salt concentration gradient in the solution near the interface was not stable enough in the horizontal configuration employed. A magnetic stirrer bar was therefore introduced into the solution reservoir to keep the salt concentration almost constant at the interface. The results were then analysed by eqn. (2):

$$\frac{c}{c_0} = \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (\text{Ref. 1}) \quad (2)$$

This yielded diffusion coefficients that were almost constant but unexpectedly high, with an average value of $3.0(\pm 0.4) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. There was insufficient time to repeat the experiment.

Although the structures of soft agarose gels of low concentration (<1 wt%) have been investigated by several techniques,²⁻⁴ stiff gels of concentration as high as 3 wt% have received much less attention. There is evidence, however, that they contain a high concentration of crystalline junction zones between domains.^{2,5} This may well affect the value of the salt diffusion coefficient. Drusas *et al.*⁶ have also reported a high D value of $2.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for a 3% agar gel. However, Rüegg and Moor⁷ have recently stated that their preliminary salt diffusion runs with agarose gels did not differ significantly from those with agar gels, and the mean value of D they obtained with 3% agar gels at 25°C was $1.68 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Their sodium chloride concentrations ranged from 1 to 4 wt%. It is interesting that even this value was higher than that for sodium chloride in water ($1.48 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Ref. 8)), although one would have expected diffusion in a gel to be somewhat slower.⁹

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11

The Prediction of Diffusivities and Diffusion-related Transport Properties in the Drying of Cellular Foods

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SUMMARY

Natural solid foods are made of cellular tissues. A fully predictive method to obtain effective diffusivities for the purpose of modelling drying processes is based on the properties of these structures. The method requires a simplified composition data bank and a physical properties data bank, the latter including binary molecular diffusivities, densities, membrane and cell wall permeabilities, molecular weights and water viscosity and molar volume. The procedure is based on calculating volume fractions, mass conductivities, tortuosities and water chemical potential for each phase.

NOMENCLATURE

- A defined by eqn. (18)
- B defined by eqn. (21)
- C defined by eqn. (20)
- D diffusivity (m s^{-2})
- \mathcal{D} binary diffusion coefficient (m s^{-2})
- f z-component of vector function f
- k membrane permeability ($\text{kg kmol m}^{-1} \text{s}^{-1} \text{kJ}^{-1}$)
- K^u mass conductivity based on chemical potential driving force ($\text{kg kmol m}^{-1} \text{s}^{-1} \text{kJ}^{-1}$)
- l characteristic length (m)
- m mass (kg)
- $n_{\beta\lambda}$ z-component of the outwardly directed unit vector normal to the $\beta\lambda$ interphase (m)

p	pressure (Pa)
P'_κ	cell wall permeability (m^2)
R	ideal gas law constant ($\text{J mol}^{-1} \text{K}^{-1}$)
s_b	bulk shrinkage coefficient
t	time (h)
T	temperature (K)
u	parameter given by eqn. (21)
V	volume (m^3)
w^*	shrinkage velocity (m s^{-1})
x	mol fraction
X	moisture content (kg water per kg dry matter)
X^*	moisture content within an averaging volume (kg water per kg dry matter)
z	prevailing drying direction (m)
β	constant used in eqn. (20)
γ	constant used in eqn. (20)
ε	volume fraction
η	viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)
μ	chemical potential (J mol^{-1})
ρ	density or mass concentration (kg m^{-3})
τ	tortuosity
ϕ	relative humidity
χ	tortuosity as defined in eqn. (8)
ω	weight fraction

Subscripts

a	air
eff	effective property
i	constituent i
j	constituent j
m	combined membrane property
p	plasmalemma
P	proteins
s	non-aqueous materials
st	starch
t	tonoplast
w	water
0	reference state
β	generic phase

γ intercellular space

η cytoplasm

κ cell wall

λ generic phase

ν vacuolar phase

Superscripts

0 β phase reference state

* local equilibrium property

Symbols

$\langle \rangle$ spacial volume average

INTRODUCTION: CELLULAR FOOD SYSTEMS

Modelling of transport phenomena in foods has been primarily in two ways. One, assuming total mass transfer control in a medium which was treated as homogeneous, its heterogeneity being accounted for by the use of effective diffusivities. The other, acknowledging the influence of heat and mass transfer, and treating the medium as non-shrinking and porous. One example of the first was Jason's (1958) pioneer work on fish drying. One early example of the second approach is found in King (1968).

Natural solid foods are made of cellular tissues, which are very peculiar porous systems. Figure 1 illustrates a simplified vegetable tissue, where the cells have been changed into a simpler multiphase structure. Actual cells are more complicated, as indicated in Fig. 2. The cell wall consists of cellulose

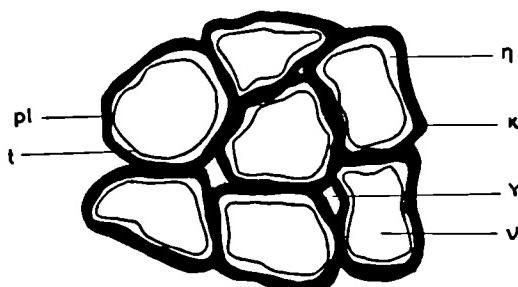


Fig. 1. Simplified cellular tissue. (pl, plasmalemma; t, tonoplast; v, vacuole; η , cytoplasm; γ , intercellular space; κ , cell wall.)

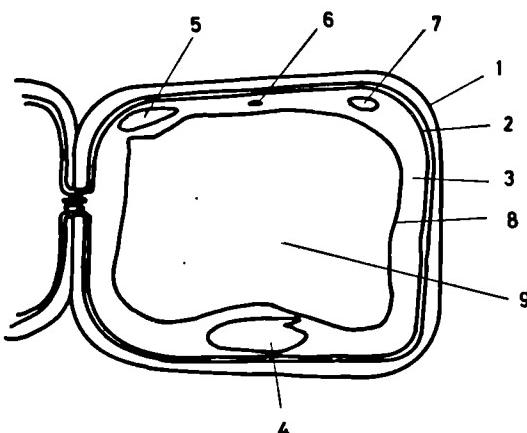


Fig. 2. A less simplified sketch of a cell. (1, cell wall; 2, plasmalemma; 3, cytoplasm; 4, nucleus; 5, chloroplast; 6, mitochondrion; 7, amyloplast; 8, tonoplast; 9, vacuole.)

microfibrils embedded in a matrix of hemicellulose with a cementing layer rich in pectins. Depending on the extent of dehydration, water is found here as a liquid phase in a capillary force field or as adsorbed water. The cytoplasm is bounded externally by the plasmalemma and internally by the tonoplast. The cytoplasm contains a variety of metabolic, respiratory and other functional organelles, and it is connected to adjoining cells by cytoplasmatic strands, plasmodesmata. For simplicity, it will be considered as a single phase, which is reasonable in terms of water relationships. It is made primarily of proteins and water, although it contains starch, lipids, sugars, salts and other compounds. Depending on the amount of water, it will appear as a fluid or as a gel. The water content of the vacuole is the highest of all the phases described in Fig. 1; it is contained essentially as a true solution of sugars, organic acids and inorganic salts, although there is some colloidal material. The differential permeability of the membranes gives the cell unique properties; the vacuolar water is held by an osmotic field which results in the intercellular spaces containing only water vapour and which produces turgor pressure. In addition, the deprivation of water results in an accompanying change of volume. As an example, the bulk shrinkage coefficient of apples ($s_b = V_b/V_{b,0}$) was found by Lozano *et al.* (1980) to be

$$s_b = 0.11X + 0.17 \quad (1)$$

Thus, when dried to $X=0$ the final volume is 17% of the initial volume, an extent of shrinkage which it is hardly justifiable to neglect.

MASS TRANSPORT EQUATIONS

Using a volume-averaging procedure, the following equation is obtained for unidimensional drying (Crapiste, 1985; Rotstein, 1986):

$$\langle \rho_s \rangle \left[\frac{\partial X^*}{\partial t} + w^* \frac{\partial X^*}{\partial z} \right] = \frac{\partial}{\partial z} \left(\langle \rho_s \rangle D_{\text{eff}} \frac{\partial X^*}{\partial z} \right) \quad (2)$$

This equation is obtained after a number of simplifications, which include neglecting the contribution of thermal diffusivity on physical grounds, several deviation terms on geometrical grounds and the assumption of local equilibrium. In eqn. (2) X^* identifies the moisture content of an averaging volume associated with its centroid:

$$X^* = \frac{\langle \rho_w \rangle}{\langle \rho_s \rangle} \quad (3)$$

so that the moisture content of a sample of volume $V(t)$ is given by

$$X = \frac{\int_{V(t)} X^* \langle \rho_s \rangle dV}{m_s} \quad (4)$$

Here $\langle \rho_w \rangle$ and $\langle \rho_s \rangle$ are the space averages of water and non-aqueous constituents, respectively, and m_s is the total solids content of the sample. The shrinkage velocity w^* is defined as an average of the velocity of all non-aqueous constituents over the $1, \dots, M$ phases:

$$\langle \rho_s \rangle w^* = \sum_{\beta=1}^M \langle \rho_{s\beta} v_{s\beta} \rangle \quad (5)$$

D_{eff} , the effective diffusivity, is the principal component of the effective diffusivity tensor in the direction of drying.

THE PREDICTION OF EFFECTIVE DIFFUSIVITIES

It has been shown (Crapiste, 1985; Rotstein, 1986) that the effective diffusivity is related to the mass conductivity and the water chemical potential dependence on moisture content. If K_{eff}^μ is the principal component of the effective mass conductivity,

$$D_{\text{eff}} = \frac{K_{\text{eff}}^\mu}{\langle \rho_s \rangle} \left(\frac{\partial \mu^*}{\partial X^*} \right)_{T^*} \quad (6)$$

where it is assumed that there is an equilibrium relationship of the type

$$\mu_w^* = \mu_w^*(X^*, T^*) \quad (7)$$

The effective mass conductivity tensor is made up of the contributions of phase mass conductivities corrected by phase volume fractions and tortuosity. This is physically analogous to the well-known definition

$$D_{\text{eff}} = D_{ij} \frac{\epsilon_\gamma}{\chi} \quad (8)$$

for a porous medium, where ϵ_γ is porosity (or air volume fraction) and χ is tortuosity as defined on the basis of eqn. (8). However, in this treatment the mathematical representation is different (Crapiste, 1985; Rotstein, 1986). In one dimension

$$K_{\text{eff}}^\mu = \sum_{\beta=1}^M K_\beta^\mu (\epsilon_\beta + \tau_\beta) \quad (9)$$

where τ_β is the newly defined tortuosity for the unidimensional case:

$$\tau_\beta = \sum_{\substack{\lambda=1 \\ \lambda \neq \beta}}^M \frac{1}{V} \int_{A_{\beta\lambda}} n_{\beta\lambda} f_{\beta\sigma} dA \quad (10)$$

ϵ_β is the volume fraction of the β phase, $n_{\beta\lambda}$ is the component in the direction of drying of the outwardly directed unit vector normal to the $\beta\lambda$ interphase, and $f_{\beta\sigma}$ is the same direction component of a vector function that can be obtained analytically. Because K_β^μ and ϵ_β can be predicted and $f_{\beta\sigma}$ may be calculated, the effective mass conductivity is a property which can be fully predicted. By proper modelling, eqn. (7) is also amenable to theoretical calculation, thus making feasible the prediction of D_{eff} .

PREDICTION OF PHASE MASS CONDUCTIVITIES

Starting from the point mass continuity equation, it is possible to obtain relationships to predict phase mass conductivities.

The different phases have been described in the Introduction. In the case of the vacuolar phase, considering it as a true solution,

$$K_v^\mu = \frac{\rho_v \mathcal{D}_{ws}}{(1 - W_w)} \left(\frac{\partial \mu_{wv}}{\partial \omega_{wv}} \right)_{p_v T_v}^{-1} \quad (11)$$

which results from using the usual constitutive equation for diffusion and taking into account that at constant temperature

$$(d\mu_{wv})_{T_v} = \left(\frac{\partial \mu_{wv}}{\partial \omega_{ws}} \right)_{p_v T_v} d\omega_{wv} \quad (12)$$

In eqn. (11) \mathcal{D}_{ws} is the binary diffusion coefficient for a system consisting of water and a solute. To give a value to \mathcal{D}_{ws} a satisfactory model is needed for the vacuolar solution. It has been shown (Crapiste, 1985) that a glucose solution is a reasonable representation.

The mass conductivity of the cytoplasm phase, K_η^μ , can be calculated using an equation analogous to eqn. (11), the nature of the solution being different from that of the vacuolar solution, as described in the Introduction. The resulting value is a conductance which must be added in series to those of the two membranes, plasmalemma (k_p) and tonoplast (k_t), to obtain an overall membrane permeability, k_m :

$$\frac{1}{k_m} = \frac{1}{k_p} + \frac{l_\eta}{K_\eta^\mu} + \frac{1}{k_t} \quad (13)$$

The mass conductivity of the air phase, which occupies the intercellular space, is approximated considering the case of water vapour diffusion in a stagnant phase (Crapiste, 1985; Rotstein, 1986):

$$K_y^\mu = \frac{\rho_y M_a}{R^2 T^2} \frac{\omega_{wy}}{(1 - \omega_{wy})} \mathcal{D}_{wa} \quad (14)$$

where \mathcal{D}_{wa} is the binary diffusion coefficient of a water-air gaseous system.

The cell wall mass conductivity describes a type of flow which is better described by Darcy's law (Crapiste, 1985). Thus

$$K_\kappa^\mu = \frac{\rho_\kappa P'_\kappa}{V_w l_w} \quad (15)$$

where P'_κ is the cell wall permeability.

All the required diffusivities and permeabilities have been retrieved from the literature (Crapiste, 1985; Rotstein, 1986) and used to calculate the phase effective mass conductivities shown in Fig. 3.

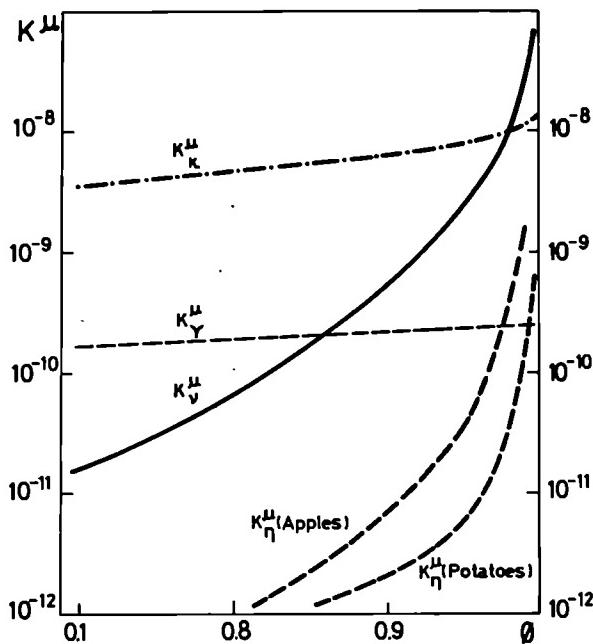


Fig. 3. Mass conductivity coefficients of cell wall (K), intercellular space (γ), vacuole (v) and membrane system (η).

PREDICTION OF VOLUME FRACTIONS

Volume fractions are predicted on the basis of densities. Thus, on the basis of an approximate representation of the different phases and literature data, it is possible to predict the volume fraction of each phase. The density of vacuolar solutions can be approximated by that of sugar solutions, the density of the cytoplasm can be predicted taking into account the concentration of proteins and starch in the corresponding foodstuff, the density of the cell wall results from data for cellulose and that of the gas phase from use of the ideal gas law. In addition, to obtain volume fractions there is a need to know the bulk density of the food material as a whole. So far these data can only be obtained experimentally. Lozano *et al.* (1980, 1983) provided this information for apples and potatoes over the entire range of moisture contents. The experiments involved are simple and straightforward. Crapiste (1985) presented predicted vacuolar, cell wall, cytoplasm and intercellular space volume fractions for apples and potatoes.

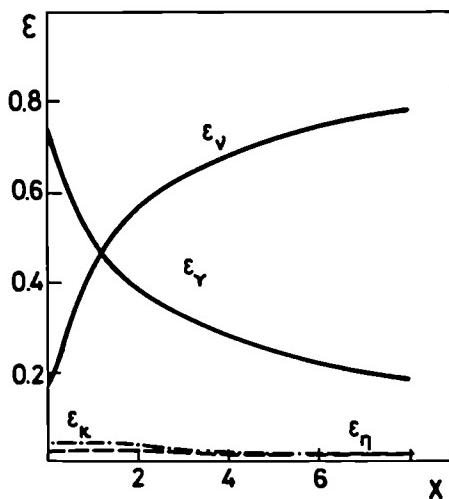


Fig. 4. Volume fraction of vacuole (v), intercellular space (y), cell wall (κ) and membrane system (η).

The results for the case of apples are reproduced in Fig. 4. They are in reasonably good agreement with experimental data from Lozano *et al.* (1980, 1983).

PREDICTION OF TORTUOSITIES

In the simple unidimensional case, the tortuosity is obtained analytically, solving the differential equation:

$$\frac{d^2 f_\beta}{dx^2} = 0 \quad \beta = v, \eta, \kappa, y \quad (16)$$

with suitable boundary conditions. Crapiste (1985) has calculated tortuosities for the different phases of apple tissues. Results for the vacuolar phase are shown in Fig. 5.

WATER CHEMICAL POTENTIALS IN THE DIFFERENT PHASES

The prediction of equilibrium water chemical potentials on the basis of the cellular tissue characteristics was studied by Rotstein and Cornish (1978) in

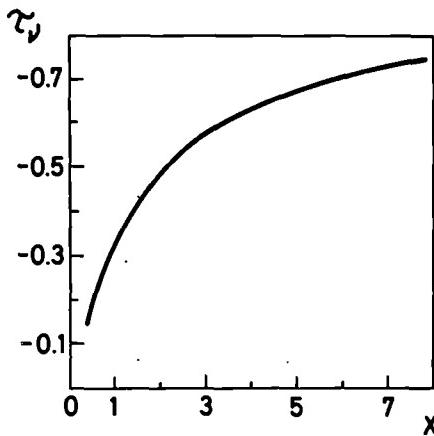


Fig. 5. Vacuolar tortuosity.

the context of the prediction of sorptional equilibrium of fruits in moist air. This work was extended by Crapiste (1985) to include other foodstuffs. Table 1 summarises the equations recommended for evaluating water chemical potential.

Equation (17) is an approximation based on considering all sugars as glucose. Essentially the argument of the logarithm is mole fraction times activity coefficient. Thus, if using glucose is in conflict with compositional evidence, the activity coefficient must be replaced by one representing the prevailing composition. The quantities B , β and γ in eqns. (20) and (21) depend on temperature. They can be found in Kelsey (1957). For the cytoplasm the prevailing constituents are proteins; in addition, there may be starch in foods such as potatoes. Thus, two equations are given, eqn. (22) for starch and eqn. (23) for proteins.

A FULLY PREDICTIVE METHOD

From the above it can be concluded that it is possible to predict effective diffusivities for the purpose of modelling the process of drying cellular foodstuffs. The procedure is summarised in Fig. 6. Two data banks are needed. One provides a simplified representative composition of cellular foodstuffs, indicating the contents of the more important sugars, starch and any other significant constituent. Experience indicates that there is no need to go into too much detail. For instance, for apples it suffices to indicate the

TABLE 1
WATER CHEMICAL POTENTIAL IN THE DIFFERENT CELLULAR PHASES

<i>Phase</i>	<i>Recommended equation</i>	<i>Source</i>
Vacuole	$\frac{(\mu_w - \mu_{w0})_v}{RT} = \ln [x_{wv} 10^{A(1-x_{wv})^2}]$	(17) 1
	$A = 1.274 - (635.840/T)$	(18)
Cell wall	$\frac{(\mu_w - \mu_{w0})_k}{RT} = \left[\ln \frac{X_k - u}{X_k} + C \right]$	(19) 2,3
	$C = \gamma \left[\frac{0.489}{X_k + 0.489} \right]^{1/3}$	(20)
	with u from	
	$(X_k - u)(B - u) = \beta u^2$	(21)
Cytoplasm	$\frac{(\mu_w - \mu_{w0})_c}{RT} = \ln [1 - \exp(-bX_{st}^c)]$	(22) 2,3
	$b = -53.4759 \quad c = 2.3015$	
	$\frac{(\mu_w - \mu_{w0})_p}{RT} = d_1 \omega_p f \exp(d_2 \omega_p)$	(23) 2,3
	$d_1 = -0.08896 \quad d_2 = -6.9173 \quad f = -1.2303$	
	$\omega_p = \frac{X_p}{1 + X_p}$	(24)
Intercellular space	$\frac{(\mu_w - \mu_{w0})_g}{RT} = \ln \phi$	(25)

Sources: 1, Rotstein and Cornish (1978); 2, Crapiste (1985); 3, Rotstein (1986).

sugar (as glucose), proteins, cellulose and water content. For potatoes the sugar content is the same way, starch, proteins, cellulose and water. The other data bank contains physical properties such as binary molecular diffusivities, cell wall and membrane permeabilities, water partial molar volume and viscosity, densities of the different solutions and bulk densities as functions of moisture content.

In addition, four subroutines are built. Subroutine EPSILN uses the density and composition data to calculate phase volume fractions. Subroutine MASCON calculates phase mass conductivities by means of

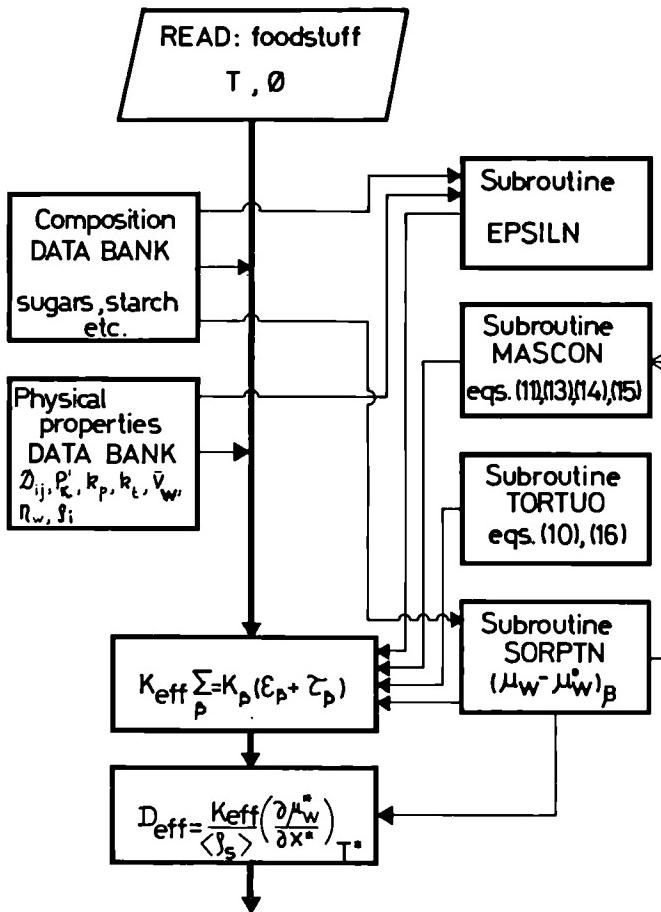


Fig. 6. Flow diagram of effective diffusivity prediction method.

eqns. (11), (13), (14) and (15). Subroutine TORTUO finds phase tortuosities solving the problem given by eqn. (16) and using eqn. (10). Subroutine SORPTN provides water chemical potentials for each phase and the tissue, calculating the partial derivatives

$$\left(\frac{\partial \mu_\beta}{\partial \omega_\beta} \right)_{p_\beta, T_\beta} \quad \text{and} \quad \left(\frac{\partial \mu_w^*}{\partial X^*} \right)_{T^*}$$

Equations (9) and (6) are used to evaluate K_{eff}^μ and D_{eff} .

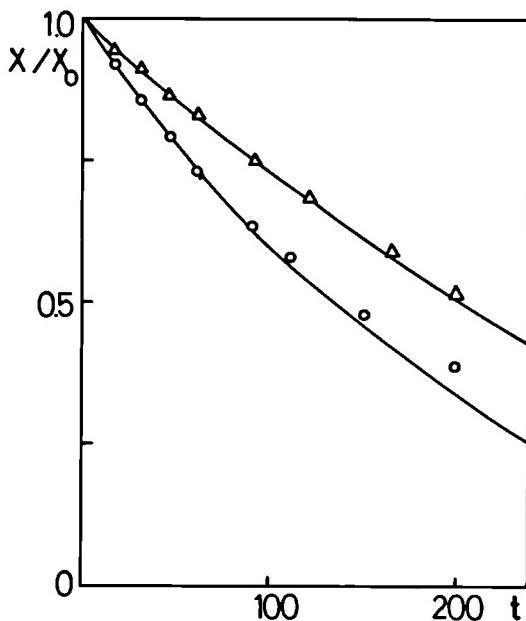


Fig. 7. Predicted and experimental drying performance of apples. Air velocity, 2 m s^{-1} ; air temperature, 28°C . Δ , $\phi = 0.438$; \circ , $\phi = 0.284$.

EXPERIMENTAL AND PREDICTED RESULTS

Crapiste (1985) used the predictive procedures above to solve a theoretical model for isothermal drying. Figure 7 shows experimental and theoretical results for air drying of apples at $\phi = 0.438$ and $\phi = 0.284$, with an air velocity 2 m s^{-1} and temperature 28°C . It can be seen that the predictive method provides good estimates of drying performance, although the estimates start to depart from experimental data as moisture content decreases. This is to be expected since at low moisture contents the membranes become non-functional and the characteristics of the structure change.

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DISCUSSION

H. Schubert spoke for many participants in asking if there was any experimental evidence from real materials to compare with the predictions or analysis made possible by this very interesting model. *E. Rotstein* confirmed that he had used the model to estimate diffusivities and predict drying rates. Reasonable correlations had been obtained in experiments on apples, potatoes and pears.* In particular, predictions of porosities were well confirmed by experiment. The correctness of predictions of, say, tortuosities could not be assessed directly but the consequent correlation between measured and predicted diffusivities did so indirectly. *C. Cantarelli* also congratulated the speaker and asked him if there were any points of contact with solvent extraction of components—oils, sugars, pigments, for example—from vegetable materials. He assumed that the model was not applicable to meat because cellulose was largely absent from meat. *Rotstein* said that regarding the former he was in contact with most other workers in the field and hoped for good progress on those aspects. On the applicability of the model to meats, the absence of cellulose was no problem and he was currently working on adapting it to that group of materials. *M. Roques* found the approach most impressive and asked what size of averaging volume was used. How many cells would there be in it? *Rotstein*: Smaller

* This additional material, especially Fig. 7, is now included in the text of the chapter—Ed.

than the volume of the sample considered, larger than the volume of the system unit which in this case was the individual cell. In practice, the algebra is evaluated but no actual decision of that kind was made. He did not wish to oversell his approach and emphasised that there was no conflict between his approach and that commonly adopted. In practice, as dehydration proceeds, the number of live cells decreases and that of dead cells increases until eventually the system becomes that conventionally assumed. At this point his model could be expected not to apply. In fact, it seems to work further in that direction than expected.

J. B. Gros: Why is the tortuosity factor here negative and less than unity? Secondly, did you use a different model from that of Margules to evaluate activity coefficient from the liquid concentration? *Rotstein:* Effective diffusivity is usually defined so as to be less than molecular diffusivity because of the smaller cross-section. Diffusion is then molecular diffusivity $\times \epsilon$ and the path is more tortuous so the diffusivity is *divided* by the tortuosity which is normally positive and <1 . In his case the smaller cross-section is accounted for by ϵ as usual, but the effect of tortuosity is provided for by an additive term, τ (in eqn. (9), for example), which must accordingly be less than unity and negative to account for the physical conditions. This is not an arbitrary choice, but is necessitated by the particular analysis and mathematical relationships in the model. Regarding activity, he commended the 'building block' approach. In this case he used a particular relationship to represent activity coefficient which appears to work satisfactorily for sugary or starchy foods such as fruits, potatoes, rice and sweet potatoes. In the case of animal products it might be beneficial to use a different model for each module of the system. The aim is always to use the simplest model, of course. *I. M. V. Adams:* Can the solutions for different tissues be combined additively—as for example in animal tissue? *Rotstein:* The *kind* of vegetable cell was not important in this model, mainly the relative proportions of the components. The case of animal tissue was, as stated before, under consideration currently and he would prefer not to try to anticipate its outcome for the present.

12

Vapour Component Selectivity when Drying Porous Solids Wetted with Liquid Mixtures

[A summary, based on a recording of the brief verbal presentation of E. U. Schlünder (BFE, Karlsruhe, Federal Republic of Germany) and miscellaneous publications submitted by him subsequently, prepared by Ronald Jowitt]

In a closed system, the composition of the vapour in equilibrium with a binary liquid mixture differs from that of the liquid except at the azeotrope composition, when they are the same. Vapour–liquid equilibrium diagrams such as Fig. 1—for isopropanol–water—are used to represent these compositions at specified temperatures (30°C in the case of Fig. 1), \tilde{x}_1 and \tilde{y}_1 being, respectively, the molar fractions of isopropanol in the liquid and vapour phases. The diagonal line denotes the same molar fractions in the vapour and liquid phases, and the curve corresponds to the actual equilibrium molar fractions over the range 100% water to 100% isopropanol.

If the whole of, say, a 50 mol % mixture of the two liquids were evaporated, the vapour would, of course, also contain 50 mol % of each, but if a small fraction of the mixture was evaporated the vapour would contain ca 60 mol % of isopropanol and the liquid would be depleted in that component. If evaporation continued in this way the vapour would continue to be richer in alcohol than the remaining liquid, which would be progressively depleted in alcohol until the whole had been evaporated. At the azeotrope, the composition of vapour and liquid is the same and evaporation (or condensation) proceeds as if the liquid were of a single molecular species, but at alcohol concentrations above the azeotropic composition the vapour contains less alcohol than the liquid and water is preferentially lost, leading to a progressive increase in alcohol content in the remaining liquid. These phenomena are widely used to enable liquid mixtures to be fractionated and separated, notably in the petroleum and chemical industries, in circumstances where only the liquid and vapour are normally present in the equipment.

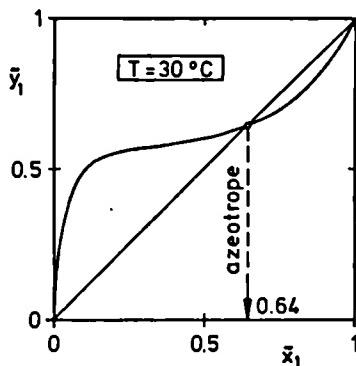


Fig. 1. Vapour-liquid equilibrium for isopropyl alcohol (1)-water (2) at 30°C.

When evaporation takes place into a gas such as air, the same relationships do not apply because the different components then have to diffuse through the gas phase (Fig. 2). Analysis of this case (Turner and Schlünder, 1986) shows that if the gas leaves saturated with both components equilibrium conditions prevail and selectivity depends only on the relative volatilities, as shown in Fig. 3. If the contact time is insufficient for thermodynamic equilibrium to be reached but the evaporation rate is low and liquid-side mass transfer coefficients are large, selectivity depends on gas-side mass transfer and relative volatility, and may be water- or alcohol-selective, depending on conditions, except in the particular case where the higher volatility of alcohol is just offset by its slower diffusivity relative to water, when the evaporation is non-selective and the vapour composition and the liquid composition have the same 'pseudoazeotropic'

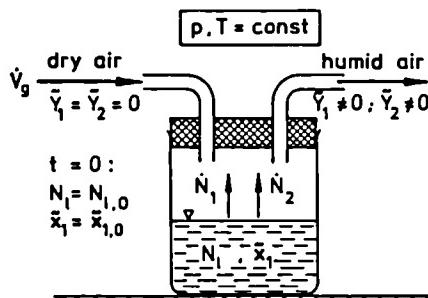


Fig. 2. Evaporation of a binary mixture from a free liquid surface.

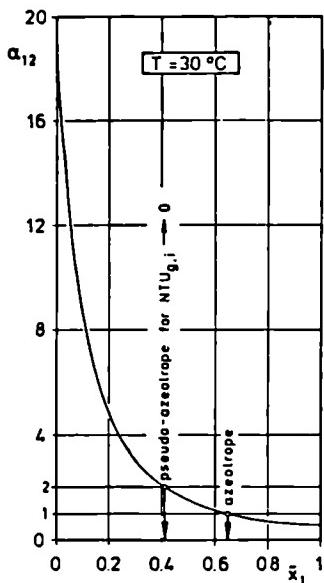


Fig. 3. Relative volatility for isopropyl alcohol(1)-water(2) at 30°C.

value—in this case, 41 mol % alcohol. If the contact time is still insufficient for equilibrium to be reached but either the evaporation rates are high or liquid-side mass transfer coefficients are low, evaporation is non-selective and the vapour composition is the same as that of the liquid.

When the liquid is evaporated during the drying of porous solids, liquid-side mass transfer is by diffusion, not by convection as in the preceding case, and interaction between the solid and the liquids might also occur. In the system shown by Fig. 4 (Schwarzbach, Nilles and Schlünder, 1987) and represented by Fig. 5, a steady-state concentration profile is established of penetration depth z^* . If the thickness, $L \gg z^*$, and the profile is established (5–10 min), then evaporation is non-selective (a certain degree of selectivity might occur initially before the profile is established). If $L \ll z^*$, selectivity is again dominated by relative volatility and gas-side mass transfer conditions. However, as Fig. 6 indicates, penetration depths are of the order of 0.15–1.5 mm. Figure 7 shows the selectivity for propanol (S_1) calculated for different L/z^* ratios (\bar{x}_{1SSA} is the pseudoazeotropic composition) and Fig. 8 the corresponding measured selectivity using plates of different thicknesses and porosities (ε).

At high alcohol concentrations, the expected absence of selectivity is

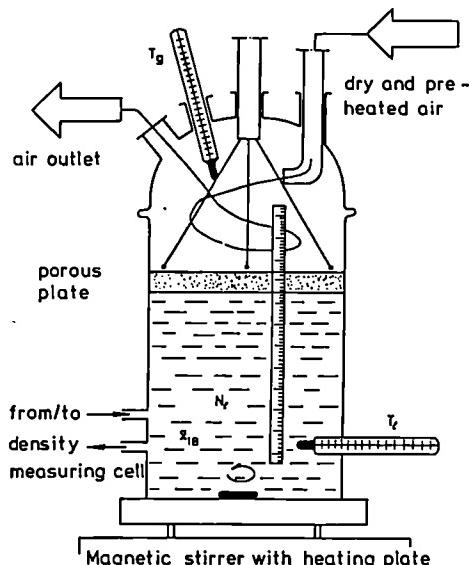
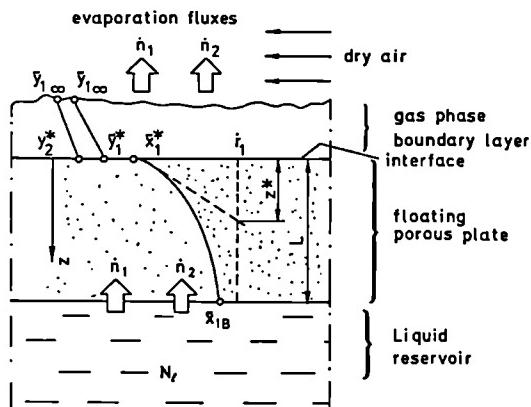


Fig. 4. Experimental apparatus I.

observed but at lower concentrations an unexpected degree of selectivity is seen with even the thickest plates, indicating at first sight diffusivities some $10^4 \times$ greater than normal (10^{-5}). Alternatively, intense microconvection in the pores could account for the effect. Figure 9 shows the effect of pore size alone and the anticipated suppression of the effect of such microconvection with the finest pore size ($1 \mu\text{m}$). This microconvection is

Fig. 5. Concentration profile $\tilde{x}_1(z)$ in a porous plate, floating on a liquid reservoir.

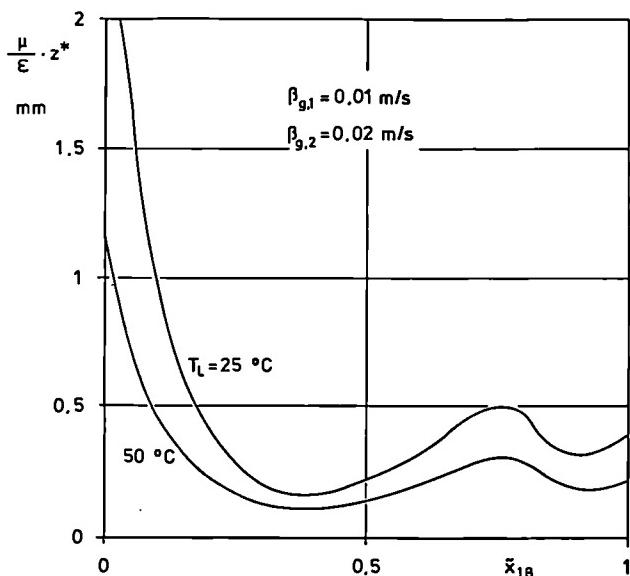


Fig. 6. Penetration depths for 2-propanol–water, evaporating into dry air, at two different temperatures.

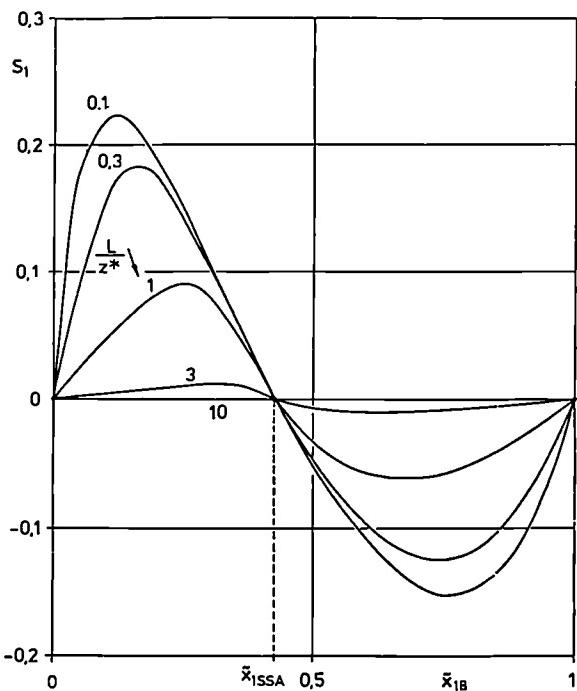


Fig. 7. Selectivity versus mole fraction of evaporating 2-propanol–water at different ratios L/z^* .

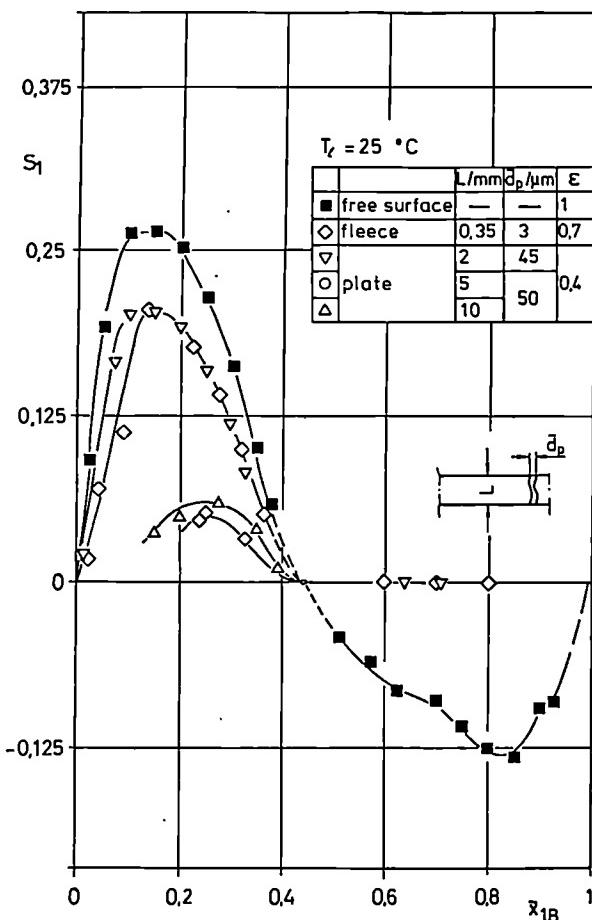


Fig. 8. Selectivity S_1 versus mole fraction \bar{x}_{1B} for plates of different thickness L at 25°C .

attributed to the Marangoni (and to a lesser extent the Bénard) effects which occur when negative surface tension (and density) gradients exist between the bulk and the surface of the liquids in the pores. The relative effect of surface tension gradient ($d\gamma_{s1}/dz$) and density gradient ($d\rho_1/dz$) can be seen by comparing Fig. 10 with the experimental results in Figs 8 and 9, II indicating that the bulk liquid is *above* the porous plate and evaporation takes place from the lower surface. The existence of the intense convection in the pores can be demonstrated by applying a soluble dye to the 'drying'

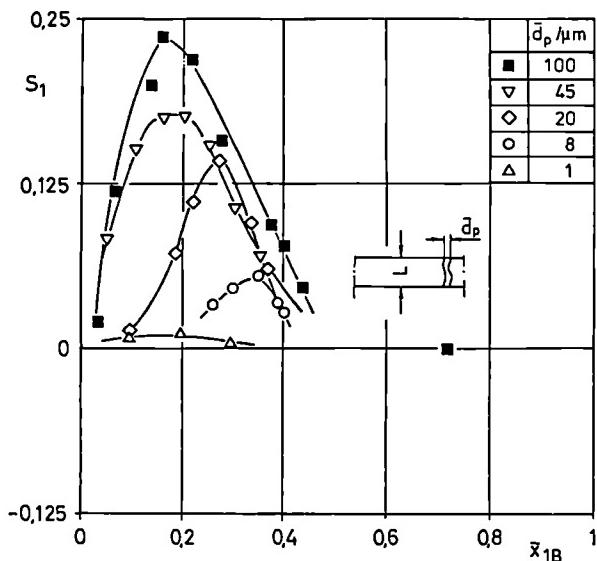


Fig. 9. Selectivity S_1 versus mole fraction \bar{x}_{1B} for plates of different pore size, $L = 2 \text{ mm}$, $\varepsilon = 0.4$, $T_i = 50^\circ\text{C}$.

Set-up	(I)		(II)	
	a	b	a	b
mole fraction	$\bar{x}_{1B} < \bar{x}_{1SSA}$	$\bar{x}_{1B} > \bar{x}_{1SSA}$	$\bar{x}_{1B} < \bar{x}_{1SSA}$	$\bar{x}_{1B} > \bar{x}_{1SSA}$
concentration profile				
$\frac{dg}{dz} \cdot \frac{dp_t}{dz}$	(-)	(+)	(+)	(-)
$\frac{dy_{g,t}}{dz}$	(-)	(+)	(-)	(+)

Fig. 10. Stability diagram for the different arrangements.

side of the plate. In cases Ib and IIb no selectivity occurs and no penetration of the dye takes place, but in cases Ia and, to a certain extent IIa, where selectivity occurs, the dye is instantly transferred through the plate to the liquid.

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DISCUSSION

W. E. L. Spiess felt that the work described, although not itself concerned with foods, had clear implications for evaporation from aroma-containing foods and called for further study in relation to them. *E. U. Schlünder* said that his question earlier in the Seminar on whether cheese was a solid was meant to elucidate the system as either a continuous solid in which the liquid was immobilised, or a porous one in which the liquid phase was present as a more-or-less mobile liquid. Their tests had covered ternary mixtures, including for example glycerine, to assess the influence of viscosity on these effects. Their findings would be published later. *G. D. Saravacos* suggested that equilibrium thermodynamics might explain these effects in terms of the relative volatility or activity coefficient of the organic component. At these dilute concentrations propanol, for instance, would have a very high relative volatility compared to that of water, in which case the liquid diffusivity of propanol to the surface would be controlling until the azeotrope concentration was reached. If this were so, then by using hexanol or ethyl acetate (important in food systems), for example, instead of propanol, the effect should be increased. *Schlünder* had so far only used propanol but intended extending the work to other volatile organics.

However, they were satisfied that the effect would be the same and their explanation would still apply whatever the volatile and its volatility. Briefly, as the drying rate is always high enough and the porous plate is always thick enough, the evaporation rate is always liquid diffusion controlled regardless of the fugacity or relative volatility, high or low. As the volatility of the propanol at low concentrations is so very high the surface becomes rapidly depleted in it and a concentration profile develops within the porous plate which stabilises to a quasi-static state condition. As the penetration depth of this profile is less than the thickness of the plate, then a mass balance around the plate can be made. The penetration depth of this profile decreases considerably as the drying rate increases so that inside the pores there is hydraulic flow towards the interface and back-diffusion of alcohol or water. If such a condition, which depends only on drying rate and plate thickness, can be established, then it is perfectly non-selective on either side of the azeotrope composition if the pores are very small—about 1 μm .

Part 2

ELECTRICAL PROPERTIES

13

Electrical Properties of Foods: A General Review

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INTRODUCTION

Electrical properties of foods are of general interest as correlates of their physical and chemical attributes, and are of practical interest in optimisation and control of dielectric heating processes. A substantial data base on research during the past several decades by investigators from many disciplinary fields shows that the primary determinants of electrical properties of food are frequency, temperature, chemical composition and physical structure. Among the most intensively investigated food properties have been the relative dielectric constant and loss factor, i.e. the real and imaginary parts of complex permittivity. These basic dielectric properties determine some related electrical properties which affect how energy is coupled from an electromagnetic wave travelling in free space and how this energy is distributed in an irradiated material. The aim of this chapter is to review the current state of information on electrical properties of foods related to their physical and chemical state, and to their microwave heating characteristics. The material summarised in the present chapter is detailed in Refs. 1–4.

BASIC PROPERTIES

Electrical properties of food of basic interest are their dielectric constant and loss relative to free space, or the real and imaginary components of relative complex permittivity. These properties have been investigated for many food materials over a period of nearly four decades by scientists

interested in the internal state of biological materials and in the effects of electromagnetic energy on living systems. A more pragmatic basis for engineering interest in electrical properties of foods is their role in dielectric heating processes at radio and microwave frequencies. The development of radar during the Second World War and the discovery that energy at high frequencies caused internal heating of biological materials stimulated considerable interest in electromagnetic interactions in biological systems and their effects in dielectric heating processes. In this section, research on the dielectric properties of foods and their major biochemical constituents will be reviewed as the basis for considering some predictive models of dielectric behaviour as a function of chemical composition, frequency and temperature.

Basic Measurements

Measurement of food properties at submicrowave frequencies (i.e. frequencies less than those of 'microwaves') began nearly four decades ago. Dunlap and Makower, for example, found that the dielectric constant and conductivity of dehydrated carrot were influenced at frequencies from 18 kHz to 5 MHz by moisture content, frequency, temperature, density and particle size.⁵ Similar results were found by other investigators for various food products. Variations in dielectric constant and loss indicating post-harvest changes in physiological state during storage were also found.

Dielectric measurements at microwave frequencies at temperatures above and below freezing showed sharp differences in dielectric behaviour between the frozen and unfrozen states, which were then related to runaway heating effects by Morse and Revercomb.⁶ Harper *et al.*⁷ found all dielectric losses of several meats and fruits at temperatures below freezing to decrease with increasing frequency and decreasing temperature. Measurements on meat and fish by Bengtsson *et al.*⁸ showed losses of minced samples to be intermediate between those of unminced samples with fibres perpendicular or parallel to the applied field, indicating anisotropic behaviour. These and many other dielectric measurements prior to the 1970s are summarised in an annotated bibliography compiled by Goldblith and Decareau in 1973.⁹

Many dielectric measurements of the past two decades were by the standing wave method of Roberts and von Hippel¹⁰ in research initiated by Goldblith and von Hippel at Massachusetts Institute of Technology (MIT) in cooperation with various investigators. Slotted line techniques were also used by Nelson and his co-workers at the US Department of Agriculture. A major centre for food measurements was established at the Swedish

Food Institute (SIK), based on the cavity perturbation method of Risman and Bengtsson.¹¹ Methods at the Torry Research Station in Aberdeen also included time-domain spectroscopy and stripline techniques.

Measurements at MIT were made on liquid and solid food products such as potato, meats, milk and oils,¹²⁻¹⁶ in addition to more fundamental studies on food constituents as a basis for predictive models of dielectric behaviour. Materials measured at SIK included meats, fish, fruits, vegetables, soups, bouillons and gravies at temperatures above and below freezing.¹⁷⁻¹⁹ The comparison of standing wave measurements at MIT with cavity perturbation measurements at SIK for foods at similar frequencies and temperatures has shown close agreement between the two methods. Nelson and co-workers at USDA have studied dielectric properties of agricultural products such as grains, fruits and vegetables.²⁰⁻²³ A review of the electrical properties of many agricultural products was published in 1973 by Nelson.²⁰ Measurements at the Torry Research Station by Kent have been mainly on frozen fish.²⁴⁻²⁷ Various studies by other investigators relating to the development of models of the dielectric behaviour of foods will also be reviewed.

Moisture Content

Water is one of the major constituents of foods and is known to contribute to dielectric behaviour of rotational interactions with an electromagnetic field which have significant dispersion characteristics from low to high frequencies. Standard dielectric measurements on water by Cook²⁸ and von Hippel²⁹ agree with predictions by the Debye model of static and optical dielectric constants and critical wavelengths of pure polar solvents as a function of temperature from 0 to 75°C are provided in a classic study by Collie *et al.*³⁰ The importance of water in the dielectric behaviour of food was recognised by many because of variations in dielectric constant and loss with moisture content. Studies by de Loor and Meijboom³¹ and de Loor³² on potato, potato starch and milk over 1.2–18.0 GHz are of particular interest, since Cole–Cole plots of their results corrected for anomalous conductivities show that high-moisture foods are essentially linear dielectrics with single relaxations at microwave frequencies and that relaxations of bound water and other dipolar constituents at sub-microwave frequencies can be neglected in predictive models for dielectric behaviour of such foods. Relaxations at MHz frequencies in protein solutions had been reported, for example, by Takashima³³ and Schwan.³⁴ Measurements by Stuchly³⁵ on granular solids at 9.4 GHz from –20 to 120°C showed the temperature dependence of moist solids to increase with

moisture content, but showed little or no variation with the temperature of the dried solids measurements, an interesting result in terms of its implications for modelling food properties.

Ash Content

Although conductivities were reported in early measurements on foods, their significance in determining dielectric behaviour was not generally recognised for nearly three decades. Van Dyke *et al.*¹⁵ reported increased losses in minced beef with increasing salt content and decreasing losses with increasing fat content. This led to a study of cation binding³⁶ effects which showed that the major monovalent and divalent cations in milk—potassium and calcium—were in partially associated and dissociated states, as shown by atomic absorption and ion-selective electrode measurements. This suggested that the ash content of foods was also partly associated and dissociated. A second study on milk showed that its dielectric properties could be predicted by correcting Debye's model for dielectric constant depression due to water binding by dissolved salts and for enhancement of dielectric loss factor by conductivities measured as sodium chloride equivalent solution.¹⁶ These effects of dissolved salts on the depression of the dielectric constant and increase of dielectric loss in aqueous ionic solutions had been described elegantly in a classic paper by Hasted *et al.*³⁷ These corrections may also be applied to the prediction of dielectric behaviour in liquid food systems, e.g. milk, fruit juices, gravies, by means of the modified Debye model. One of the points to be emphasised in considering the effects of dissolved salts is that the temperature dependence of ionic conductivity is positive, i.e. it increases with temperature, and that of the loss factor of water below the critical frequency is negative. Thus salt concentration may have a significant effect on the temperature dependence of aqueous ionic solutions, because the total dielectric loss factor has a dipole component which may have negative temperature dependence and an ionic component that always has positive temperature dependence. Accordingly, total dielectric loss may decrease initially as the temperature is raised and then increase as the temperature is increased further. The crossover point, i.e. the temperature at which the total loss begins to increase with temperature, is known to vary with concentration of dissolved salts.

Organic Compounds

The effect of organic compounds in semi-solid foods, in contrast to the

effects of dissolved salts in an aqueous ionic solution, is to depress both dielectric constant and loss by the exclusion of dielectrically-active aqueous ionic fluids from such foods of the same volume as those of pure ionic solutions. The values of the dielectric properties of organic food constituents are much smaller than those of aqueous ionic fluids. This is seen in measurements on fats, oils and food solids, which show typical values of less than 5·0 and 0·5 for dielectric constant and loss, respectively, which are relatively constant over a range of frequencies and temperatures.³⁸⁻⁴⁰ Measurement of one oil over an extended frequency range suggested a dispersion region above 10 MHz and one or more relaxations between 100 MHz and 2 GHz.¹³ The values for organic food solids are similar to values obtained from measurements on many organic compounds in von Hippel's Laboratory for Insulation Research by Westphal and are relatively constant over frequency and temperature ranges normally involved in microwave processing of food.

Non-interactive Mixtures

On Kent and Jason's premise that dielectric behaviour of food is essentially determined by moisture and salt content,⁴¹ liquid and semi-solid foods may be modelled as non-interactive binary mixtures of aqueous ions and organic food components. Dielectric properties may then be predicted by mixture theory. One model for complex permittivity was derived from Fricke's model⁴² for the complex conductivity of a colloidal suspension. The modified Fricke model is based on treatment of the food system as a two-phase mixture whose solid phase properties are approximated by typical organic solid values and whose liquid phase properties are modelled by the Debye equations corrected for dissolved salt concentration. Both the Fricke and the modified Fricke models involve phase volume fractions and a shape factor to take account of departure from spherical shape of the suspended particles. For oblate spheroidal particles randomly orientated in the field the equation reduces to the Maxwell form for spheres with a shape factor of one and Rayleigh forms for long cylinders parallel to the field with a shape factor of two. The modified Fricke model⁴³ predicted dielectric properties of oil-water emulsions of widely varying composition and of selected semi-solid foods⁴⁴ with reasonable accuracy. A distributive model⁴⁵ has also been used to predict the dielectric behaviour of semi-solid foods, such as meats, vegetables and liquids with high levels of suspended solids, such as orange juice. This model is obtained by lumped circuit analysis and involves the linear distribution of complex permittivities by phase volume fraction.

Interactive Mixtures

A synergistic loss effect in which loss factors of ethanol–water mixtures were greater than those of either pure component was found by Buck in 1965.⁴⁶ He attributed this effect to hydrogen bonding interactions between the hydroxyl groups of ethanol and water molecules which stabilised the liquid structure and shifted the critical wavelengths of mixtures to values intermediate between those of the pure components. Similar effects have been seen in carbohydrate–water mixtures by Roebuck *et al.*⁴⁷ While such effects are not likely in semi-solid foods, they may be of some interest in liquid systems containing alcohol or high dissolved sugar concentrations, such as wines or fruit syrups. An empirical model for such effects was derived for mixtures of methanol and ethanol with water based on calculating intermediate values of the static and optical dielectric constant and the critical wavelength in the Maxwell form of the modified Fricke model and substituting these values in the Debye models for pure polar solvents.⁴³ Measurements of methanol–water and ethanol–water mixtures at 3 GHz agreed closely with model predictions and clearly showed the synergistic loss pattern reported by Buck.

Low Temperatures

As seen in some of the measurements cited above, foods show marked differences in dielectric behaviour at temperatures above and below freezing which, in association with the temperature coefficient of the sub-zero loss factor, have been associated with runaway heating effects.^{6–8} Properties of frozen meats and fish have been measured at the Swedish Food Institute^{17–19} at microwave frequencies and of frozen fish at the Torry Research Station by Kent^{24–27} over a wider range of frequencies. The research by Kent included measurement of relaxations at low frequency, which were tentatively related to a Maxwell–Wagner mechanism, as a measure of pre-storage fish quality, and time-domain measurements at microwave frequencies which were shown to be related to physical changes in frozen fish during storage. A number of frozen meats were also measured at MIT at temperatures of –20 and –40°C and frequencies from 300 to 2450 MHz.⁴⁸ These measurements were consistent with a model based on thermodynamic equilibrium between ice and water which is used to predict the fraction of unfrozen water at various temperatures. The model gave reasonable predictions of unfrozen water levels calculated from dielectric loss measurements at both temperatures based on the pattern of loss variation with frequency. The results suggest a need to define the term ‘bound water’ in frozen foods as unfrozen water,

containing dissolved ions, which is physically entrapped by ice and solids, as distinguished from 'bound water' defined by Hasted⁴⁹ as that electrically bound to dissolved ions and solids in irrotational or rotationally hindered forms.

High Temperatures

As previously indicated, values of the dielectric properties of many organic liquids and solids are much less than those of aqueous fluids and are relatively invariant with temperature.⁴⁰ While few guidelines are available for predicting the dielectric behaviour of foods at temperatures above the boiling point of water, it is possible that their high-temperature properties are continuous with those at lower temperatures. It is also possible that the properties of biological materials show discontinuities due either to additional relaxation mechanisms or changes in ionic conductivity at high temperatures. It might therefore be of interest to investigate the possible existence of such effects with reference to high-frequency sterilisation processes.

RELATED ELECTRICAL PROPERTIES

Electrical properties of foods closely related to their basic dielectric properties are implicated in transmission and reflection of radiant energy at product surfaces and its absorption within the product. Conceptually, these properties can be used in modelling energy transmission and absorption from a plane wave travelling in unbounded free space and striking the surface of a homogeneous dielectric material at some angle of incidence. They are not so easily applied to energy transmission and absorption by foods in a microwave cavity because of impedance mismatch effects under changing load conditions affecting frequency and power levels in energy transfer from the frequency generator to the cavity, and because of multiple reflections and transmission modes which can result in appreciable standing wave effects. Recognising many difficulties in applying these relationships directly, the related properties are of interest as a means of visualising the electrophysical nature of microwave heating effects and the general effects of the dielectric behaviour of food on conditions in a microwave cavity for various load conditions and the distribution of absorbed electrical energy within the irradiated food material. The following discussion is hypothetical and provides a conceptual approach

that has been used to model time-temperature profiles and microbial lethaliities in agar slabs, cylinders and spheres similar to high moisture foods by means of finite-difference equations for conventional heat transfer with an internal heat generation term expressed in terms of dielectric properties of food. These concepts are based on electrophysical analogies described in von Hippel's classic work on dielectrics and waves.⁵⁰

Energy Transmission

The energy of a plane wave striking the surface of a dielectric material in a cavity at some random angle of incidence is partly transmitted by the material and partly reflected to the cavity, where it may be reflected from the walls back to the surface or back to the microwave generator, depending on the extent of impedance mismatch between the loaded cavity and the generator. The mismatch between free space and the dielectric is based on relative intrinsic impedances determined by the material's complex permittivity and is subject to similar variation with frequency and temperature. Organic food solids have intrinsic impedances about half that of free space (which is 377Ω) and reflect about 45% of the energy striking the surface at an angle of 45 degrees. An aqueous solution of 0.1 M sodium chloride has an impedance about one-eighth that of free space at normal temperatures and would reflect nearly 85% of the energy striking the fluid surface at the same angle. The plane wave analogy can also be used to illustrate the experimentally verifiable point that foods of low moisture content are likely to couple energy less efficiently than foods of intermediate or high moisture content. This has been demonstrated by calorimetric measurements which showed that approximately twice the volume of oil or dried solids was required to couple the same amount of energy as water or a 0.1 M aqueous ionic solution at 2450 MHz. Not to press the analogy too far, it must be said that a theoretical model for volumetric energy coupling characteristics based on food properties is not known at this time. However, coupling characteristics for a specific oven can be determined empirically for food analogues as a function of load volume, chemical composition and geometry by calorimetric measurements. The concept of impedance mismatch is most useful in visualising some effects of energy reflection and transmission at the air-food interface, e.g. the effect of standing waves on uniformity of heating. The concept also provides a rational basis for differential heating effects in heterogeneous or composite food products. It is also possible that some energy transmitted in a homogeneous food product is reflected internally at surfaces opposite the surfaces of energy incidence. This is not considered likely for intermediate

and high moisture foods of reasonable electrical and physical thickness because of the great amount of absorption taking place.

Energy Absorption

The energy of a plane wave transmitted through the surface of a dielectric is refracted towards the normal at an angle which is determined by its intrinsic impedance relative to that of air and its angle of incidence, as seen in Snell's law. The angle of refraction by organic solids may vary between 0 and 30 degrees, depending on the angle of wave incidence; that of a 0·1 M aqueous ionic solution as much as 5 degrees. This may be of concern in modelling internal heat generation based on the path length for energy absorption. As energy is transmitted along this new angle, it is attenuated according to Lambert's law based on a propagation factor which is also determined by the material's basic dielectric properties. The real part of this propagation factor is the inverse of the material's penetration depth, i.e. the depth beyond the surface at which the voltage gradient of the applied field is $1/e$ of its value at the surface, and is designated the attenuation factor. The imaginary component of the propagation factor is designated the phase factor and determines the wavelength and velocity of wave propagation in the dielectric.

CONCLUSION

This review has summarised some research on the electrical properties of foods, emphasising basic dielectric properties of interest in high-frequency food processing development. Research leading to some predictive models for these properties has been reviewed and a physical and chemical basis for such models discussed in terms of frequency and temperature response, chemical composition and physical structure. The basic dielectric properties of foods determine the related properties which affect energy transfer from an electromagnetic field and internal energy absorption by the food product. These related properties were considered conceptually in terms of possible relationship to dielectric heating effects as an approach to modelling high-frequency food processes. Some of the research on food dielectric behaviour as a physiological correlate has also been considered. Concerning the future, it might be that the next chapter in food dielectric research could be a more interesting one involving some new measures of the physical environment within foods at the molecular level and some new approaches to relating food dielectric behaviour to high-frequency heating effects, particularly for products of irregular geometry and composition.

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DISCUSSION

H. Schubert noted the absence of data correlating heating effects with size and shape of the foods. Is all now known about this? *R. E. Mudgett*: By no means! The only correlations known to him were with agar 'phantoms' made to resemble high-moisture-content foods. These had given good if not final results but they are not real foods. Low- and intermediate-moisture-content foods had not been covered and there was much still to be done. *W. E. L. Spiess* and *Schubert* noted that some results were available for spheres and slabs, and (quoted by the author himself) for cylinders. The problem remained, however, for irregular shapes. *Mudgett* concurred and all agreed that more work was needed on the subject.

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The COST 90bis Collaborative Work on the Dielectric Properties of Foods

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SUMMARY

The use of dielectric measurements in the important area of water content determination has been examined for two problem areas: (1) solutions of various sugars and (2) particulate foods. In the first case frequency, concentration and temperature were investigated, and in the second the effects of density, particle size and water content were further clarified.

INTRODUCTION

At the outset of the COST 90bis project it seemed that not much of significance could be done in collaborative measurements on the electrical properties of foodstuffs since participants had such disparate interests that little, if any, overlap occurred between them. This absence of shared interests was perhaps exacerbated by the different forms of apparatus in use and by the different frequency ranges covered. Table 1 shows this variety in detail.

Several systems can be adopted for the classification of the work in dielectric properties and each has merit in demonstrating further the varied interests of workers in this field.

I. Classification by Food Type

- (a) Liquids and suspensions, e.g. milk products and sugar solutions.
- (b) Solids, e.g. whole fruit, fish and meat.
- (c) Particulate solids, e.g. dried milk, coffee and grains.

TABLE 1

<i>Laboratory</i>	<i>Type of equipment</i>	<i>Frequency range</i>	<i>Materials of interest</i>
Torry Research Station, in collaboration with Leatherhead Food RA, UK	Waveguide bridge Three-terminal cell and time domain	8–12·4 GHz 10 Hz–25 kHz	Food powders and sugar solutions Low-temperature frozen foods (–190 to –60°C)
Electrophysics Department, Technical University of Denmark	Resonant cavity	~3 GHz	Solid biological materials
SIK, Gothenburg, Sweden	Resonant cavity	~3 GHz	Foodstuffs (0 to 100°C)
CNRS, Thiais, France	Resonant cavity	~5 GHz	Hydration effects in biopolymers
University College, Cork, Ireland	Two-terminal cell resonant circuit A.C. bridge, three- terminal cell and D.C. two-terminal cell	10, 15, 20, 25 and 30 MHz 100 kHz–5 MHz	Milk and butter
University of Athens, Greece	Thermal depolarisation currents	Not applicable	Emulsions and sugar solutions (–220 to +30°C)

2. Classification by Application

- (a) Heating by microwaves or rf, e.g. thawing or cooking of meat, fish and vegetables.
- (b) Quality assessment, e.g. shelf life of fish, meat and milk.
- (c) Moisture determination, e.g. of coffee powders, evaporated milk, sugar solutions and butter.

3. Classification by Frequency Range

- (a) D.C. conductivity, e.g. for quality of dairy products.
- (b) Low or audio frequencies (lf or af), e.g. the quality of fish and meat.
- (c) Radio frequencies (rf), e.g. for thawing and quality of frozen fish and milk.
- (d) Microwaves, e.g. for density and moisture measurement of dried milk powder, meats, fish and vegetables.

A bibliography assembled by the subgroup in which all the above aspects and more are represented contains over 200 references and it is hoped that this will be published shortly.

It is worth remembering at this point that the reason for the existence of

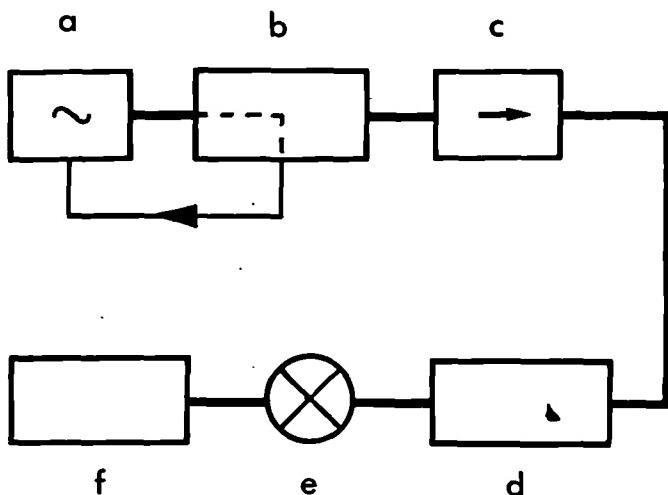
COST in general is to help European industry compete in a highly competitive world by pooling resources in certain areas. For COST 90bis this has meant cooperation in the collection and application of physical properties data. It seemed most fitting, therefore, that the resources of this small group should be directed towards the solution of certain problems encountered by the food industry in trying to apply methods based on the use of dielectric properties. One such problem area concerns the measurement of water content by dielectric methods. Within this area several problems were known, but the two topics selected for collaborative work were as follows:

1. Temperature and composition effects on the dielectric properties of sugar solutions at high temperatures in the microwave region.
2. The effects of particle size and bulk density on the dielectric properties of powdered foods in relation to moisture content and density determination.

METHODS AND MATERIALS

It must always be remembered that dielectric properties in a time-varying electric field are complex, that is to say they have two components—real, ϵ' , and imaginary, ϵ'' . The former expresses the ability of the material to store energy whilst the latter its ability to dissipate it. These two components are called permittivity and loss factor, respectively. The ratio of loss factor to permittivity is known as the loss tangent, $\tan \delta$.

Even in a given frequency range methods of measuring these properties vary and true collaborative 'ring tests' or similar comparative exercises as conducted for other physical properties are not possible. Several laboratories use resonant cavity systems for measurements in the microwave range which by their very nature restrict the users to measurements at a single frequency. In such methods a resonant cavity of known unloaded resonant frequency and Q -factor is loaded with the sample of interest (Fig. 1). If the sample has always the same geometry and volume, then the shift in resonant frequency which occurs when it is placed in the cavity can be directly related to the permittivity with some correction for the loss factor (see, for example, Ohlsson *et al.*, 1974). The loss factor itself can be determined from the change that takes place in the cavity's Q -factor. Instead of calculating the dielectric properties from these measurements such systems are often calibrated with materials of known



- a sweep generator
- b directional detector
- c isolator
- d resonant cavity
- e detector
- f SWR meter

Fig. 1. Schematic diagram of resonant cavity system for dielectric measurement (after Bengtsson and Risman, 1971).

complex permittivity. The overall accuracy to be expected is about ± 1 dielectric unit in ϵ' and ± 0.5 in ϵ'' .

Other workers use waveguide or coaxial line transmission methods, and of these only the latter could be described as truly broadband. In the case of waveguide methods the restriction in frequency range is less than in the case of resonance methods but nevertheless they are still limited, the frequency range available for measurement in the case of the so-called X-band being 8–12 GHz. The waveguide technique used in these experiments consisted of filling a section of waveguide with a known length of sample and measuring its transmission characteristic relative to that when empty.

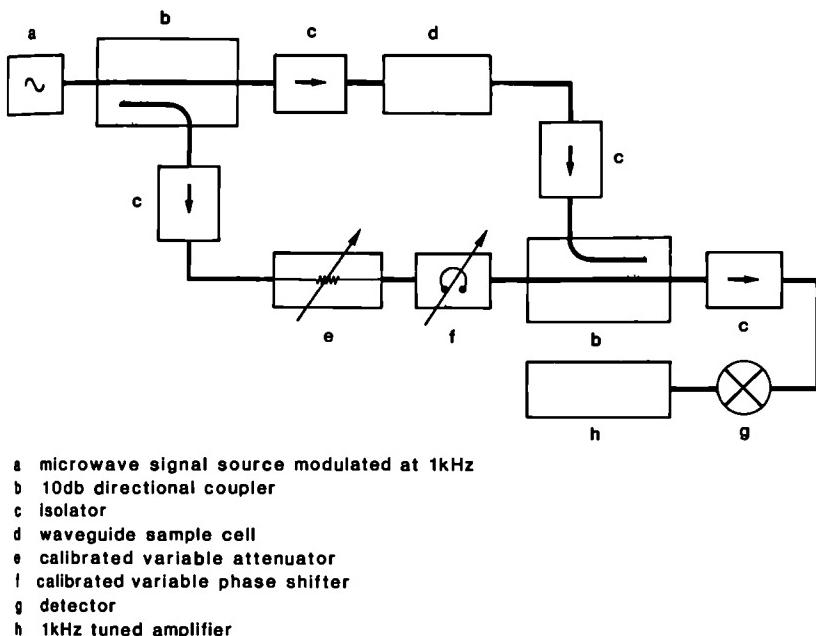


Fig. 2. X-band bridge for measurement of transmission characteristics (after Kress-Rogers and Kent, 1987).

For the measurements on powders where density was a variable, the sample of known weight was progressively compressed to measured degrees to yield data on the bulk density dependence of the dielectric properties. In this case prior knowledge is required of the number of wavelengths to be expected to traverse a given length of sample. This was easily obtained by removing small quantities of the sample without changing the density and observing the effect on the attenuation and phase shift as the sample length shortened. These two transmission characteristics were measured using the vector null balance bridge shown in Fig. 2. The incremental change in phase shift per unit length so obtained could be used to determine the overall phase shift in a sample of known length and approximately known permittivity. It was also noted that over the range of moisture contents encountered the phase shift per unit mass was practically constant, thus giving a further check on the measured value.

Errors in phase measurement are negligibly small, the greater error occurring in the measurement of attenuation. This can be markedly affected by residual standing wave effects, especially when measuring the empty cell

for reference. The resultant error in ϵ'' arising from an uncertainty of ± 0.25 dB could be as high as $\pm 5\%$, depending on the magnitude of the attenuation measured. This error decreases as the attenuation increases, but at high attenuations the precision variable attenuator in the bridge becomes more inaccurate with an uncertainty of $\pm 3\%$, causing similar fractional errors in ϵ'' . The error in ϵ' , on the other hand, is in the region of $\pm 1\%$.

Using coaxial line transmission in a similar fashion with samples of known length enables a wider range of frequencies to be examined since a coaxial line effectively propagates all wavelengths and is thus broadband. For the data reported here the technique of measurement used was one in which the frequency was swept from 2 to 18 GHz, the propagation characteristics being measured by a network analyser (HP 8409B) (see Kent and Meyer, 1983). The problem of indeterminate phase does not occur in this case because at the lowest frequency the sample length is very much less than the wavelength. Only as the frequency increases does this become a problem, but it is easily solved by noting that over the whole frequency range the dependence of total phase shift on frequency is a continuum without step changes at multiples of 360° .

In the case of sugar solutions it was necessary to devise a cell in which the length of the sample could be varied. Two such cells were constructed, one based on a triplate transmission line and the other simply a section of waveguide with appropriate sealing windows. In this method the X-band bridge was still used but the transmission characteristics were measured as a function of sample length. This was varied by introducing measured small amounts with a syringe. With the shorter path lengths there was a problem with standing wave effects inevitably caused by reflections at the sample boundaries, but as the length and hence the overall loss increased so these standing wave effects were reduced. In these transmission methods the dielectric properties can be calculated from the propagation terms α and β in the following manner:

$$\epsilon' = \frac{\beta^2 + \beta_c^2 - \alpha^2}{\beta_0^2}$$

$$\epsilon'' = \frac{2\alpha\beta}{\beta_0^2}$$

where β_0 is the free space phase constant given by

$$\beta_0 = \frac{2\pi}{\lambda_0}$$

where λ_0 is the free space wavelength. β_c is the phase constant for the 'cut-off' wavelength in the waveguide which for the fundamental transmission mode in a rectangular cross-section waveguide is given by $2 \times$ the breadth. For coaxial lines, or similar structures transmitting so-called TEM (transverse electric and magnetic) waves as in an unbounded medium, there is no cut-off wavelength.

Descriptions of all the techniques used are to be found in Risman and Bengtsson (1971), Kress-Rogers and Kent (1987), Kent and Meyer (1983), Henry and Berteaud (1980) and in a general review by Hadi *et al.* (1975). The complex dielectric properties of sugar solutions (sucrose and dextrose) and 'glucose syrup' (hydrolysed starch of dextrose equivalent by optical rotation = 42) were measured at concentrations of 20–76% solids in the temperature range of 30–70°C and at frequencies of 2·8, 3·05, 5·04, 8·5 and 11·5 GHz.

In addition, measurements were made at 2·8 and 3·05 GHz on carrageenan gels (Genugel LCI, Hercules Ltd) with sucrose added according to the composition shown in Table 2.

The complex permittivity of confectionery moulding starch was measured over a frequency range from 2 to 18 GHz at a temperature of 30°C using the swept frequency network analyser described briefly above.

Milk and 'instant' coffee powders and potato granules were measured at 10 GHz using the vector-null balance bridge mentioned earlier.

The coffee, starch and milk powders varied in moisture content from 0 to 10% (dry basis) and ranged from loosely-packed powders to compressed pellets. The potato granules were maintained at a constant equilibrium moisture content of 9% (determined by oven drying at 101°C for 24 h) but had been sieved to produce samples with particle sizes of >250 µm, >500 µm, >670 µm and >1000 µm. Two instant coffee powders differing in particle size range were produced by grinding. The potato powders were

TABLE 2
PERCENTAGE COMPOSITION OF THE
CARRAGEENAN GELS USED IN THESE
EXPERIMENTS

<i>Water</i>	<i>Sucrose</i>	<i>Carrageenan</i>
90	9	1
80	19	1
70	29	1
50	49	1

provided by W. Bergthaller of the Bundesforschungsanstalt für Getreide und Kartoffelverarbeitung, Detmold. The other powders were provided by the Leatherhead Food RA.

SUGAR SOLUTIONS

As already mentioned, a widely used method for determining the water content of foodstuffs (and many non-food materials) is the use of the selective absorption of microwave energy by water, the molecules of which, because of their strongly dipolar nature, have a relaxation frequency within the so-called microwave region (see Daniels (1967), for example). This relaxation frequency is strongly affected by temperature and viscosity. Microwave moisture determination, like many other methods, seems to be applied frequently without any knowledge of the dielectric behaviour of the subject material. Because of this lack of awareness it is usually deemed a failure when the results are not as expected. The example which motivated the work reported here on sugar solutions arose when the method was applied in the confectionery industry to sugar solutions at high temperatures and what appeared to be anomalous results were obtained. Due to a paucity of dielectric data at temperatures much above 50°C, or for solutions of greater concentration than molar, only an educated guess could be made as to why such results were obtained. It was felt that this was at least a suitable case for collaborative measurement using all the dielectric measuring resources available to the group. Some of the results are presented in Tables 3, 4 and 5, where the complex dielectric permittivity is presented as a function of sugar concentration, temperature and frequency. Also shown in these tables are data taken from published graphical presentations (Roebuck *et al.*, 1972). Some of the experimental results are plotted in the complex plane in Fig. 3, where it can be seen that an increase in concentration of sucrose produces the effects of both a reduced amplitude of the dispersion and a reduction in the relaxation frequency. All the results plotted at 5.0 GHz have been interpolated to match the temperature of measurement of the rest. The actual measured results are tabulated in Tables 3-5. It will be noted also that those at 2.8 GHz seem to differ greatly from those at the next nearest frequency of 3.05 GHz. Since those at 3.05 GHz fit better in a family of curves of permittivity versus water content, those at 2.8 GHz were not plotted in Fig. 3.

Regrettably, there are insufficient points to be able to fit any known relaxation mechanism with acceptable accuracy. The points that are

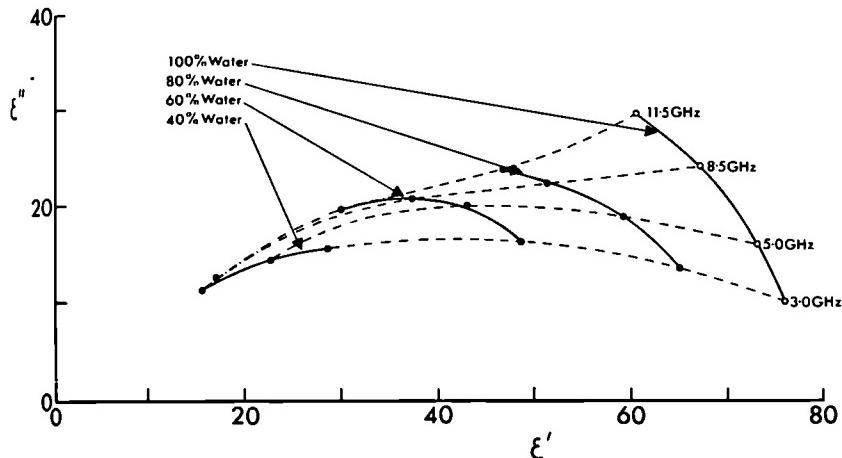


Fig. 3. Complex plane plot of dielectric properties of sucrose solutions at 30°C.
Data for water taken from Nightingale (1981).

plotted, however, are very characteristic of dipolar relaxation effects and should be compared, for example, with the results published by Suggett and Clark (1976) for various sugars, including sucrose studied at molar concentrations and at a temperature of 5°C. In that publication the relaxation spectrum was tentatively separated into three components arising from the solvent, modified solvent (bound) and solute.

The presence of relaxation mechanisms can also be displayed by plots of loss-factor measurement against frequency which show a peak at some characteristic frequency. In the presence of more than one relaxation process, however, this peak has no physical significance except as the combined effect of the various relaxations present. Even with the limited frequency range data presented here it is possible to see the effects of temperature and concentration on the relaxation peak in, for example, sucrose solutions. Figures 4 and 5 show in three-dimensional form the shifts of the relaxation peaks as temperature, frequency and concentration change. The effects due to these changes can for the sake of simplicity be associated with the viscosity which is affected by changes in both temperature and concentration. If the case is considered where only one relaxing molecular species is present, then the complex dielectric permittivity, ϵ^* , can be described as follows:

$$\epsilon^* = \epsilon_0 + \frac{\epsilon_\infty - \epsilon_0}{1 + (i\omega\tau)} \quad (1)$$

TABLE 3
DIELECTRIC PERMITTIVITY OF SUCROSE SOLUTIONS

			Temperature = 45.5°C								
5.04	60.3	14.8	46.1	37.7	27.7	15.1					
Temperature = 50°C											
2.8	68.4	7.7		60.0	11.0		39.9	10.9			
3.05	63.1	9.4		51.7	11.8		34.4	14.4			
8.5	53.3	17.1	49.0	18.7	41.5	18.3	31.4	16.6	22.5	13.7	20.2
11.5	49.4	18.2	44.0	19.1	38.0	17.7	.		17.9	11.6	14.1
									14.1	9.5	14.1
									9.5	12.4	8.1
			Temperature = 54.7°C								
5.04	58.64	12.7	46.2	16.2	37.7	16.8	28.7	14.5			
			Temperature = 65.7°C								
5.04	60.1	12.1	48.8	14.9	41.2	15.7	31.3	15.0			
			Temperature = 70°C								
2.8	63.3	5.4		55.2	7.3		41.2	8.5			
3.05	59.8	6.5		51.7	8.8		38.4	11.3			
8.5	55.9	12.8	46.4	11.5	43.2	22.7	39.7	15.7	28.1	13.8	26.5
11.5	48.9	16.3	45.4	14.5	38.2	16.3	35.8	17.3	24.0	14.4	23.3
									14.2	18.7	11.6
									15.8	11.0	15.3
									11.3		9.2
			Temperature = 90°C								
3.05	56.9	5.1	49.6	6.9			38.9	10.1			

^aData interpolated from Roebuck *et al.* (1972).

TABLE 4
DIELECTRIC PERMITTIVITY OF GLUCOSE SYRUP (HYDROLYSED STARCH)

<i>Concentration</i>	20			30		40		50		60		70		
	ϵ'	ϵ''		ϵ'	ϵ''		ϵ'	ϵ''		ϵ'	ϵ''		ϵ'	ϵ''
Frequency (GHz)														
5.04	59.1	19.5		Temperature = 26.2°C				41.3	19.5	21.4 12.7				
2.8	70.9	13.0		Temperature = 30°C				57.3	15.5	35.4 12.9				
3.05	62.6	14.4		Temperature = 36.4°C				46.7	14.4	26.8 14.1				
8.5	47.9	26.6		42.2	25.1	32.9	22.0	26.0	19.8	17.9	13.4	12.1	8.2	
11.5	41.2	20.9		35.0	22.0	31.1	20.7	23.3	16.7	16.0	11.5	10.1	6.5	
5.04	60.1	17.7		Temperature = 45.5°C				43.2	17.7	23.8 13.0				
5.04	58.3	14.2		Temperature = 50°C				44.7	15.6	25.1 13.4				
2.8	66.7	8.7		Temperature = 54.7°C				56.6	11.1	38.3 10.3				
3.05	61.6	10.5		Temperature = 65.7°C				49.1	12.7	32.3 12.7				
8.5	57.7	18.6		47.9	19.3	40.2	19.1	32.8	17.8	23.4	14.2	15.6	9.9	
11.5	43.7	21.6		43.7	19.4	35.5	17.0	27.0	15.3	18.6	10.8	13.5	8.5	
5.04	57.7	12.0		Temperature = 70°C				45.9	14.2	27.8 13.5				
5.04	56.2	10.6		Temperature = 90°C				47.9	12.4	29.1 11.8				
2.8	61.4	6.6		Temperature = 70°C				52.1	8.2	38.3 8.2				
3.05	56.9	8.2		Temperature = 70°C				46.2	9.4	35.1 11.1				
8.5	56.2	13.6		49.1	14.0	42.7	15.3	37.6	17.3	28.6	13.8	20.1	10.9	
11.5	49.0	17.7		16.2	18.0	39.6	17.3	31.0	15.3	25.2	13.4	17.4	9.4	
3.05	54.3	6.9		Temperature = 90°C				43.2	7.9	36.1 10.1				

TABLE 5
DIELECTRIC PERMITTIVITY OF GLUCOSE SOLUTIONS

Concentration	20		30		40		50		60		68	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
Frequency (GHz)												
			Temperature = 25°C									
1·0*	73·9	6·5			63·1	10·6			44·6	13·9		
3·0*	68·8	16·5			52·8	20·0			32·0	18·1		
			Temperature = 26·2°C									
5·04	60·1	20·8			42·5	21·5			22·9	15·7		
			Temperature = 30°C									
2·8	73·0	12·7			62·8	17·1			36·6	14·1		
3·05	65·0	13·3			53·6	17·6			35·8	17·2		
8·5	51·0	25·1	46·7	23·8	37·8	22·0	26·5	18·1				
11·5	48·6	28·9	46·5	26·8	33·1	20·4	23·1	16·8				
			Temperature = 36·4°C									
5·04	60·7	16·9			45·5	18·8			25·7	15·3		
			Temperature = 45·5°C									
5·04	61·0	14·4			47·0	17·4			28·5	16·1		
			Temperature = 50°C									
2·8	68·5	7·8			62·2	11·1			40·7	11·6		
3·05	64·3	8·8			55·5	13·8			39·9	15·0		
8·5	53·6	16·9	50·0	19·3	42·1	19·5	33·5	17·9	24·7	15·4	19·1	12·8
11·5	50·8	21·0	49·1	21·6	34·7	18·4	31·9	17·5	21·3	13·7	14·1	9·5
			Temperature = 54·7°C									
5·04	59·1	12·0			48·5	15·5			31·6	16·1		
			Temperature = 65·7°C									
5·04	61·3	12·6			47·9	12·4						
			Temperature = 70°C									
2·8	64·1	5·2			58·1	7·2			42·2	8·5		
3·05	59·3	5·9			52·9	8·2			45·5	11·8		
8·5	56·9	13·2	51·4	13·8	45·6	15·0	37·7	14·3	28·5	12·2		
11·5	52·5	14·7	48·3	16·5	41·1	17·2	35·2	16·1	24·9	13·0		
			Temperature = 90°C									
3·05	53·8	4·3			49·3	7·7			47·0	9·8		

*Data interpolated from Roebuck *et al.* (1972).

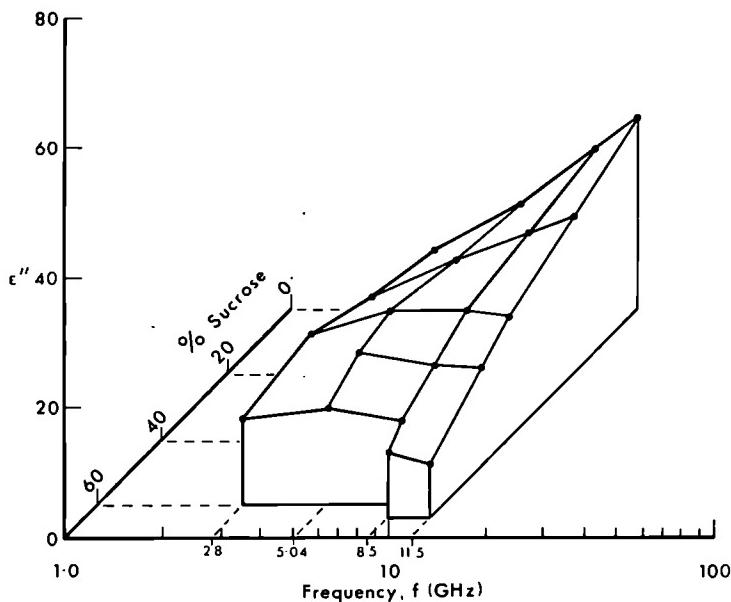


Fig. 4. Dielectric loss factor for sucrose solutions at 30°C as a function of frequency and concentration. Data at 5.04 GHz have been interpolated from the results in Table 3.

where ϵ_0 is the dielectric constant at the limit of zero frequency, ϵ_∞ is the dielectric constant at the high frequency limit, ω is the angular frequency and τ is the relaxation time, usually expressed in terms of the frequency of the peak loss factor, f_c , thus:

$$\tau = \frac{1}{2\pi f_c}$$

Classical relaxation theory describes the relaxation frequency as a function of the coefficient of viscosity η of the surrounding medium (Debye, 1929) such that

$$\tau = \frac{4\pi\eta}{KT} 3r^3 \quad (2)$$

where r is the radius of the relaxing dipolar molecule, assumed spherical. The viscosity of sugar solutions is certainly both temperature- and concentration-dependent, and hence the observed changes in the relaxation time. It is probably more correct, however, to say that dielectric relaxation

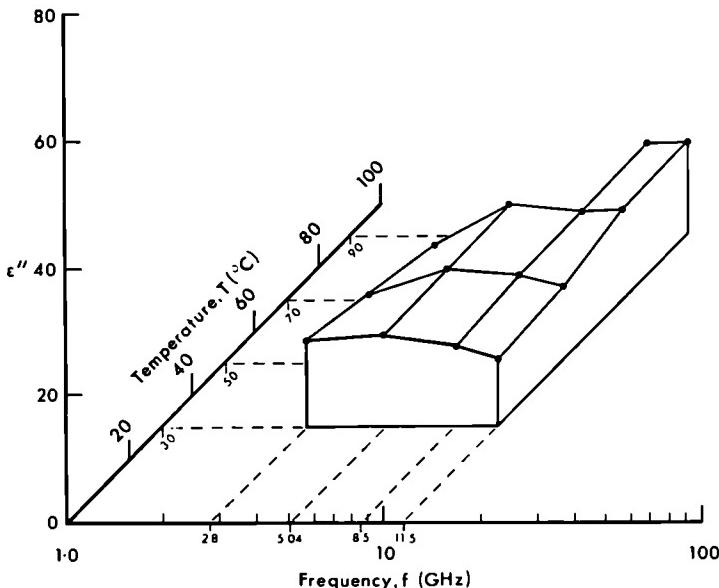


Fig. 5. Dielectric loss factor for a 60% sucrose solution as a function of frequency and temperature. Data at 5.04 GHz have been interpolated from the results in Table 3.

and viscosity are both related to intermolecular forces in the same manner. This caveat is prompted by the fact that the results obtained with the gels made up with sucrose solutions (Table 6) are indistinguishable from the results for the gel-free solutions, although the macroscopic viscosities appear to be very different. Some of these results are shown in Fig. 6, where sucrose solution results at the same frequency, temperature and water contents are plotted also. The water contents of the gels were determined by oven drying after the dielectric measurements had been made and the discrepancy between the intended composition and the measured values probably arose from evaporation of water during the preparation of the samples. The oven-dried moisture contents are the values plotted in Fig. 6.

As a second-order effect the dependence of the relaxation time on the degree of dilution must also be considered, as has been described by de Loor (1964). If from these measured dielectric properties the transmission characteristics for an unbounded medium (see below) are calculated at each of the measurement frequencies and plotted versus water content, it can be seen immediately why attenuation was unsuitable for

TABLE 6
COMPLEX PERMITTIVITY OF CARRAGEENAN GELS AS SPECIFIED IN TABLE 2

Sample (water/sucrose/carrageenan)	<i>f</i> (GHz)				Water content (oven dried)	
	2.8		3.05			
	ϵ'	ϵ''	ϵ'	ϵ''		
90/9/1	$T = 25^\circ\text{C}$	73.6	11.3	71.7	12.2	89.6
	$T = 50^\circ\text{C}$	69.0	7.4	65.0	6.9	
80/19/1	$T = 25^\circ\text{C}$	70.8	13.4	65.2	14.3	78.4
	$T = 50^\circ\text{C}$	65.8	8.3	—	—	
70/29/1	$T = 25^\circ\text{C}$	66.8	14.7	65.8	17.0	67.0
	$T = 50^\circ\text{C}$	63.0	9.1	—	—	
50/49/1	$T = 25^\circ\text{C}$	42.7	15.1	41.5	17.8	45.2
	$T = 50^\circ\text{C}$	46.8	10.9	47.0	12.2	
320/19/1	$T = 25^\circ\text{C}$	—	—	70.7	11.5	

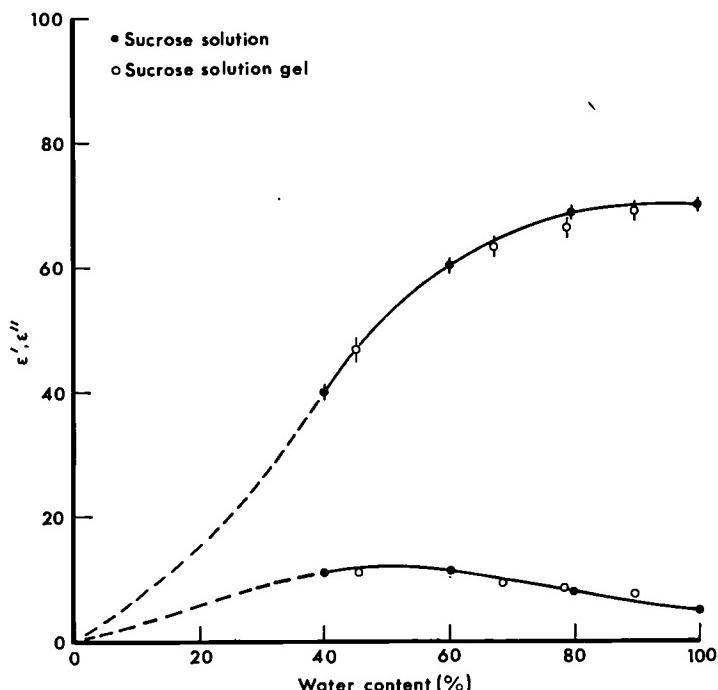


Fig. 6. Loss factor and permittivity at 2.8 GHz versus concentration for sucrose solutions at 50°C . Also shown are data collected for the carageenan gels (upper curve ϵ' , lower curve ϵ'').

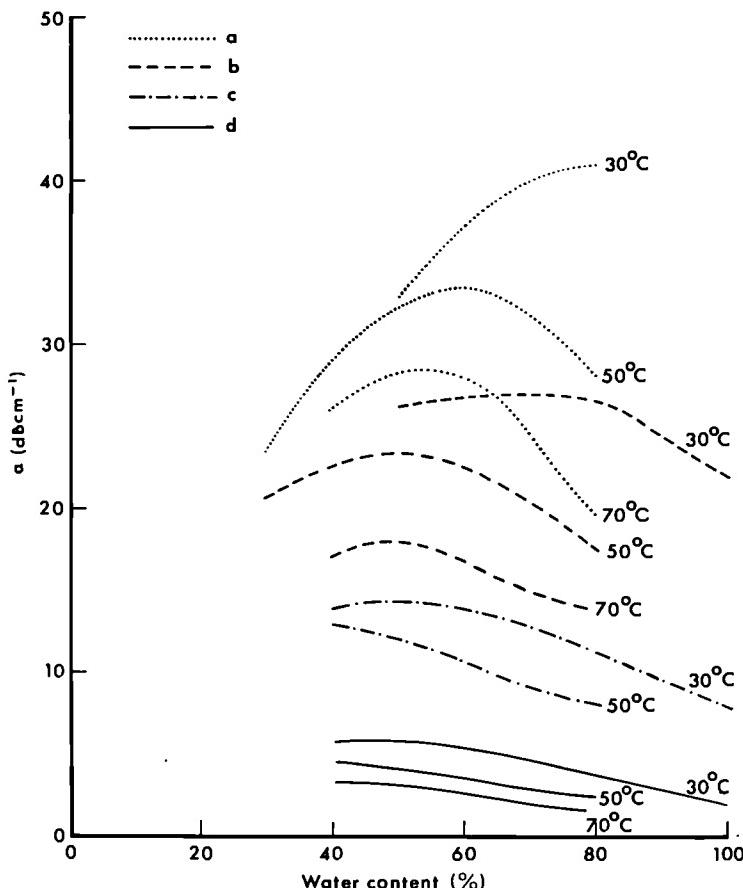


Fig. 7. Calculated attenuation per unit length versus concentration for dextrose solutions at 30–70°C. (a) 11.5 GHz; (b) 8.5 GHz; (c) 5.04 GHz; (d) 2.8 GHz.

determination of that water content (Fig. 7). Not only is it highly temperature-dependent but it is also ambiguous. Because of the shape of the attenuation versus concentration curve two possible water contents could be inferred from the same measured value of attenuation, which in any case does not vary much with concentration at the lower frequencies.

The phase shift, however (Fig. 8), demonstrates a much more uniform dependence on the concentration and clearly offers a better opportunity for unambiguous measurement of water content. Phase measurements have in fact been proposed for the measurement of water content (Ozamiz and

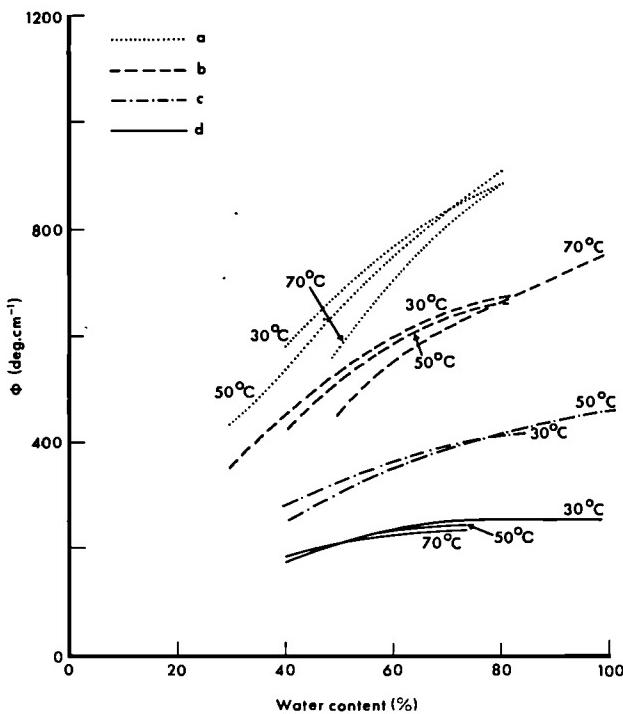


Fig. 8. Phase shift per unit length versus concentration for dextrose solutions at 30–70°C. (a) 11.5 GHz; (b) 8.5 GHz; (c) 5.04 GHz; (d) 2.8 GHz.

Hewitt, 1979) and no problem should be encountered in designing equipment for this purpose.

Although it is the results for sucrose which have been used largely to demonstrate these effects, the arguments are equally applicable to any of the results collected. Though not identical, the dependence on water content and temperature of the dielectric properties of D-glucose (dextrose) and glucose syrup (hydrolysed starch) is very similar to that of sucrose. At the lower frequencies of measurement they are virtually indistinguishable, as Roebuck *et al.* (1972) have observed.

PARTICULATE SOLIDS

Turning now to another problem area for dielectric moisture measurement, the effects of other variables such as the bulk density of powders need some

examination. Clearly, if dielectric losses are colligative then the density will be an important variable. Variation in the bulk density causes changes in the measured dielectric loss which are unrelated to fractional water content of the solid. One solution is to determine the density using some independent measurement such as the absorption of X-rays, as was proposed by Mladek (1973). This technique is in fact used in a commercial instrument but it is both costly and unpopular for food applications. It would seem unnecessary to resort to such methods when it is appreciated that the information concerning density is contained within the values for the dielectric properties. How to extract this information has been the subject of several publications (Kraszewski, 1973; Meyer and Schilz, 1980; Kress-Rogers and Kent, 1987) but, first, what of the data themselves?

Although much has been written on the dielectric properties of powders of a biophysical interest such as various proteins (see Kent and Meyer (1984)), not a great deal of attention has been directed towards powdered foodstuffs. Nelson (1984) can be considered to have contributed the most to the discussion of the properties of particulate foodstuffs in relation to their bulk density, moisture content and measurement frequency. The dielectric properties of fish meal were also discussed in this respect by Kent (1977). More recently Meyer and Schilz (1980) have described a method for the determination of moisture in powders which relies on a knowledge of the behaviour of the dielectric properties of powders as the density varies. Although similar work was published at an earlier date by Kraszewski (1973), only in the later work were the intrinsic properties of the material considered. The work of Meyer and Schilz has since been augmented by Kent and Meyer (1982) and Kress-Rogers and Kent (1987), the last-mentioned having made a detailed study of milk powder and coffee powders. In this more recent work it was shown that the function

$$R = \frac{\epsilon''}{2\sqrt{\epsilon'}(\sqrt{\epsilon'} - 1)} \quad (3)$$

derived for plane wave (TEM) propagation was to a large extent insensitive to the bulk density of a low-moisture powder (Figs. 9 and 10), and even where some residual variation with bulk density remained (Fig. 11) it was still much less than that observed in the dielectric properties ϵ' or ϵ'' themselves. Any residual bulk density dependence was shown to be eliminated by a simple iteration procedure which at the same time provides the value of the bulk density. The two-variable microwave measurement thus allows the in-line determination of a second property important in food processing rather than just the elimination of density as a

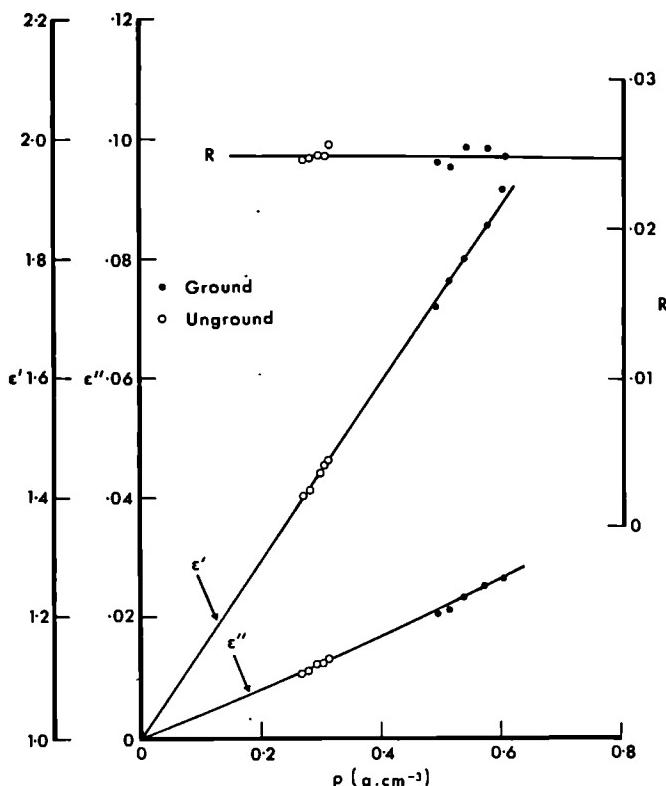


Fig. 9. Complex permittivity and ratio R (see text) versus bulk density for instant coffee powder at 25°C and 3.0% moisture content, ground and unground. This also shows the absence of any effect of particle size except for concomitant bulk density change. (After Kress-Rogers and Kent, 1987.)

complicating variable in moisture measurement. The ratio R is in fact the expression obtained by dividing attenuation per unit length by the corresponding phase shift per unit length, these two quantities being given by

$$\alpha = \frac{2\pi}{\lambda_0} \left[\frac{\epsilon'}{2} \{ \sqrt{1 + \tan^2 \delta} - 1 \} \right]^{1/2} \text{ nepers/unit length} \quad (4)$$

$$\phi = \beta - \beta_0 = \frac{2\pi}{\lambda_0} \left[\frac{\epsilon'}{2} \{ \sqrt{1 + \tan^2 \delta} + 1 \} \right]^{1/2} - 1 \text{ radians/unit length} \quad (5)$$

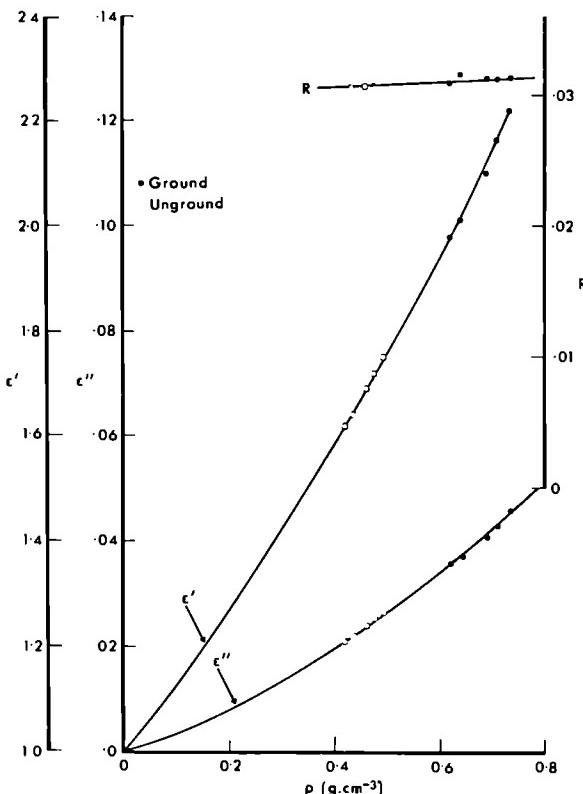


Fig. 10. As for Fig. 9 but in this case for dried whole milk powder at 4.0% moisture content. (After Kress-Rogers and Kent, 1987.)

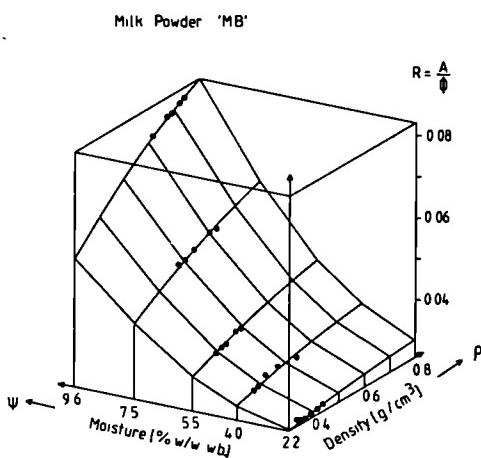
In the case of low loss, when $\tan \delta \ll 1$, then eqn. (3) results. This was the original proposition of Meyer and Schilz but they then simplified the expression even further to

$$\frac{\epsilon''}{(\epsilon' - 1)}$$

If the data collected for confectionery moulding starch over a range of moisture contents and densities are examined first, it can be seen how well the corrected measure performs as the density and moisture content change and as the frequency is swept (Fig. 12).

In this figure it can be seen that at the lowest measurement frequency R is still very much affected by the fluctuating density shown projected on to a

plane parallel to the R versus moisture content plane. As the frequency increases so R becomes much less density-dependent. The technique would appear, then, to be useful only at high microwave frequencies. This, however, is for a powder with a given particle size distribution, and the question was asked if the particle size affected the results at all. From studies on coffee and milk powders of different particle size it seems that no significant effect occurs (Figs. 9 and 10), although small changes in the



$$R = \epsilon'' / (2\sqrt{\epsilon''} (\sqrt{\epsilon''} - 1))$$

Fig. 11. The ratio $R = A/\phi$ (the attenuation over the phase shift of plane waves transmitted through the sample) as a function of moisture content and bulk density for a typical skimmed-milk powder.

results for the coffee powders were attributed to other causes such as surface changes on grinding arising from frictional heating (Kress-Rogers and Kent, 1987). The change in particle size distribution after grinding is shown in Fig. 13.

The conclusion that particle size or size distribution had a negligible effect is further confirmed by the studies performed on dried potato 'powders' of various particle sizes. The results are plotted in Fig. 14, where it can be seen that the only effect of changing this variable is to modify the bulk density. The density-independent variable R is thus unaffected.

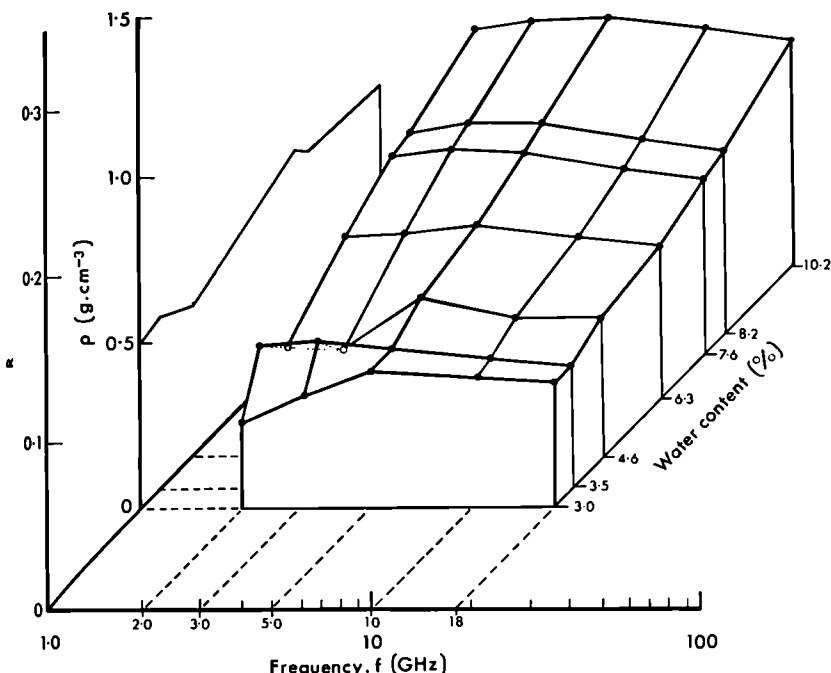


Fig. 12. Variation of ratio R with frequency and moisture content at 30°C for confectionery moulding starch. Shown also is the change in bulk density from sample to sample, which at lower frequencies is reflected in the value of R .

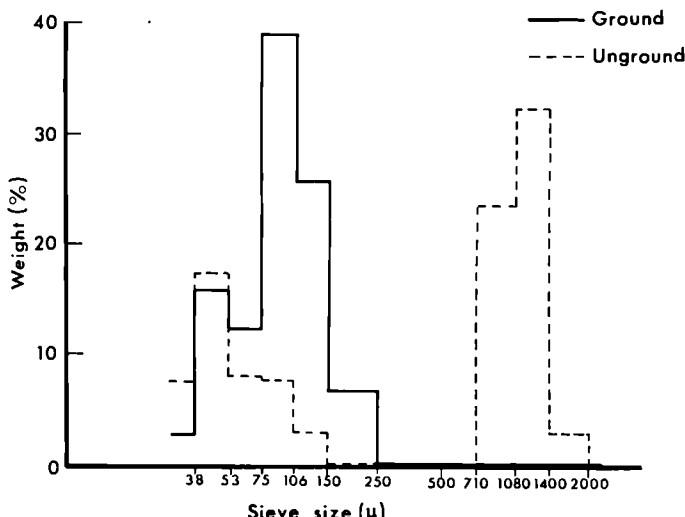


Fig. 13. Particle size distributions for instant coffee powders before and after grinding showing a bimodal distribution in the unground sample.

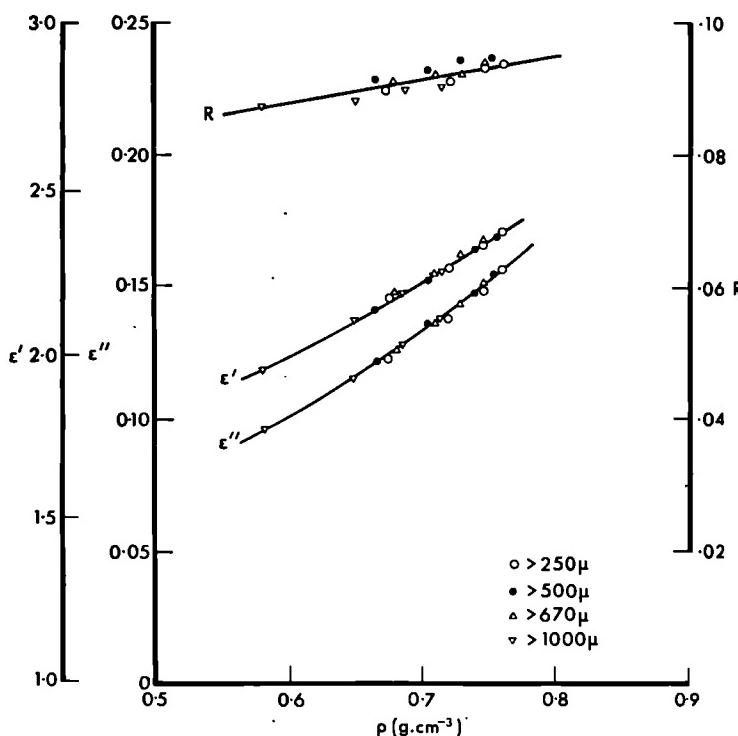


Fig. 14. Complex permittivity and ratio R for potato powders of 9% moisture content as a function of bulk density. $\circ > 250\mu$, $\bullet > 500\mu$, $\triangle > 670\mu$, $\nabla > 1000\mu$. No effect of particle size can be seen.

CONCLUSIONS

Rather more has been achieved than might have been expected from the range of interests in the 'Electrical and Optical Properties' subgroup. Firstly, it has been shown that attempts to use instrumental methods based on dielectric property measurements to determine the water content should ideally be preceded by preliminary measurements of those dielectric properties under the influence of all the likely affecting conditions. The work on sugar solutions has confirmed this view and also points to a way out of a particular problem by using phase measurement alone instead of attenuation.

Secondly, it has been shown that where both phase and attenuation are

measured, as in methods for the elimination of density dependence (particularly if the residual density dependence is eliminated by an iteration process (Kress-Rogers and Kent, 1987)), then for particulate solids those measurements are not diminished in accuracy by variations in the particle size or size distribution. In addition, it was established that the measurement frequency should be as high as possible for the most effective density compensation.

Finally, the question must be asked as to what further remains to be done. There are a number of possibilities. For example, liquids and variable bulk-density powders have been studied. It would now be appropriate, perhaps, to study the effects of porosity in foamed liquids or gels. Gels seem from this work to be a useful way of immobilising liquids for these studies without significantly affecting the dielectric properties.

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DISCUSSION

E. U. Schlünder wished to measure the *local* moisture content in, for example, a cylinder being dried. Was this possible with microwaves? *M.*

Kent affirmed that techniques were available for moisture content profiling using measurements over a wide range of frequencies followed by optimising procedures to match an assumed profile by trial and error. Such an approach had been used, for example, for remote determination of moisture profiles in soils and rocks. In a second question *Schlünder* asked if it were possible to use microwaves to determine, say, the different proportions of propanol and water present in a system. *Kent* suggested that similar multi-frequency techniques might work depending on the discrimination between the subtle differences in response of the different polar components.

Industrial Uses of Dielectric Properties of Foods

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SUMMARY

The use of dielectric properties for microwave heating applications in the food and related industries is reviewed. The importance of knowing the dielectric properties under the correct processing conditions in order to design and optimise microwave heating equipment, processes, packaging and food products is discussed and examples given. The use of dielectric measurement as a basis for microwave moisture determination in the food industry is presented and analysed. Finally, the need for more data on dielectric properties of foods is discussed.

INTRODUCTION

A knowledge and understanding of the dielectric properties of foods and other materials used in microwave heating systems is important for the successful use of microwaves in the food industry.

This statement is illustrated with the help of direct experience of a number of industrial development projects and research projects supported by the food and related industries. This survey is confined to the microwave frequency range (particularly to the two ISM frequencies 2450 and 915 MHz), the food industry and the industry supplying equipment and packaging material to it.

The dielectric property of a material consists of two components: the dielectric constant, ϵ'_r , expressing the ability of the material to store energy, and the dielectric loss factor, ϵ''_r , expressing the ability of the material to dissipate energy. Dielectric properties can be measured by the methods

reviewed by Kent and Kress-Rogers (Chapter 14). Prediction models based on composition are also available, based on considering the foods to comprise an inert food solid and a dielectrically-active aqueous solution (Mudgett *et al.*, 1977; Nelson and Russell, 1986).

The industrial use of dielectric properties can be divided into heating and measuring applications. The microwave heating characteristics of materials treated in microwave heating equipment must be known, to ensure good design and heating performance. This is important both in the construction of microwave ovens and in choosing appropriate materials for containers and packaging.

The dielectric properties of materials also form a basis for understanding the importance of product variables such as composition and geometry to the heating performance of foods. Dielectric properties are also essential for analysing the influence of important characteristics and variables such as microwave power level, frequency and temperature in microwave heating processes.

Dielectric measurements can also be used for process control, notably in-line measurement of water content. At low to moderate moisture content, microwave attenuation can be used as a measure of the water content. The number of industrial installations is limited, probably because of the great sensitivity to changes in processing variables which are difficult to control. At high water contents the method gives insufficient resolution. Using dielectric measurements, the prospects for accurately measuring the water content of different foods can be analysed and the influence of different variables can be clarified (see Chapter 14).

MICROWAVE HEATING CHARACTERISTICS

Materials

In order to design microwave heating equipment, utensils and packaging which will perform properly in practice, the microwave heating characteristics of the materials used must be known. Such characteristics depend on the dielectric properties and their dependence on temperature, composition, etc.

In the construction of microwave ovens, plastic materials and rubber are used for conveyor belts and food support shelves. These should have low dielectric losses so that they are heated to only a small extent, even during extensive use and wear. In high-temperature applications, the tendency for the dielectric losses of many plastic materials to increase rapidly when close to their softening temperatures must be considered.

Understanding of the dielectric properties is also important for the proper design of leakage prevention devices in ovens and for temperature sensors. In these a plastic dielectric material is used to prevent the propagation of microwaves by total reflection at the interface between dielectric and metal.

Food packaging for use in microwave heating operations must be selected from materials of low dielectric losses which can withstand temperatures up to 125–135°C which can develop locally in the microwave heating of foods. More rigorous requirements apply to utensils used for cooking foods in domestic microwave ovens, since these are intended for extended use.

Information on dielectric properties of plastic, rubber and other materials is often supplied by the manufacturer. It can also be found in reference handbooks, but the values are seldom given for the frequencies used for microwave heating, or over the temperature range encountered in microwave food heating applications. Measurements of the dielectric properties at the actual frequency and temperatures to be used will make the selection of non-metallic materials for ovens and packaging easier and safer.

Foods

Penetration

For a better understanding of the microwave heating characteristics of food, the dielectric properties of various foods and how these depend on composition, temperature, frequency, etc., need to be known. This awareness led the microwave oven industry in Sweden to sponsor projects on dielectric measurements and their interpretation. In Fig. 1, the dielectric properties of a number of foods over a temperature range of –20 to +60°C are shown. For practical use in the industry, the dielectric properties are converted to an attenuation factor or its inverse, the penetration depth, which defines the depth into the material at which the energy has decreased to $1/e$ ($\approx 37\%$) of its surface value:

$$d = \frac{\lambda_0}{\pi \cdot \sqrt{8} \cdot \sqrt{\sqrt{\epsilon_r'^2 + \epsilon''^2} - \epsilon'}}$$

where λ_0 is the wavelength in air (122 mm for 2450 MHz).

The penetration depth is used to interpret the affect of the water and salt content on the microwave heating characteristics of different foods. The important contribution of the salt (or other ion) content of foods on the

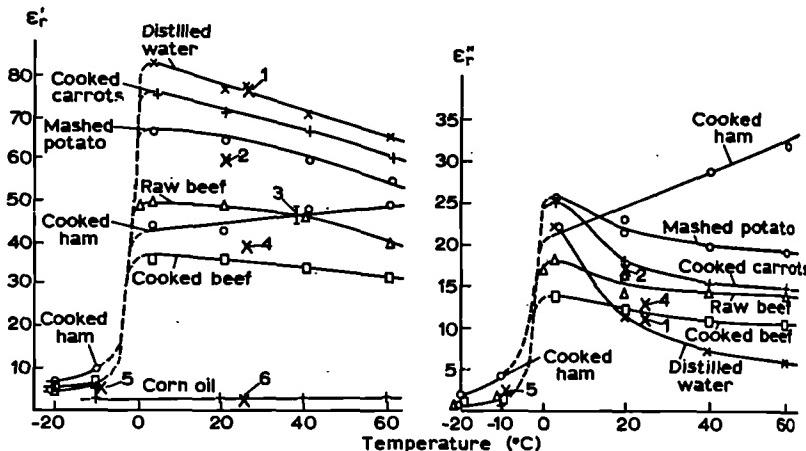


Fig. 1. The temperature dependence of the dielectric constant and loss factor for various foods (Bengtsson and Risman, 1971).

penetration depth is illustrated in Fig. 2. Most foods, for example peas and beef, have a salt content of 0.5–1%. The corresponding penetration depth at 2450 MHz is in the range of 10–15 mm at temperatures from 0 to 100°C. In ham with 3–4% salt content, the penetration depth is limited to 3–5 mm. This is quite different from the behaviour of water, where the shift to higher frequency of the relaxation frequency with increasing temperature will tend to decrease dielectric losses and thus increase the penetration depth. At 2450 MHz and at high temperatures, the polarity of the water molecules will be strengthened by the dissolved ions. There is also an increasing contribution to electric resistance heating from the dissolved ions.

At lower frequencies, the influence of the dissolved ions is even more important. Ohlsson and Bengtsson (1975) showed that at 915 and 434 MHz the penetration depth in beef at temperatures above +60°C is close to the penetration depth at 2450 MHz, although the wavelength in air is much longer and the penetrating ability would be expected to be much greater. Thus the benefit of better microwave penetration at 915 MHz in microwave tempering and thawing, which is a major industrial application, is quite limited at higher temperatures. This has limited the industrial use of 915 MHz in high-temperature microwave heating applications.

Distribution

One of the major difficulties of microwave heating is that the temperature distribution inside the food is difficult to control. Hot and cold spots

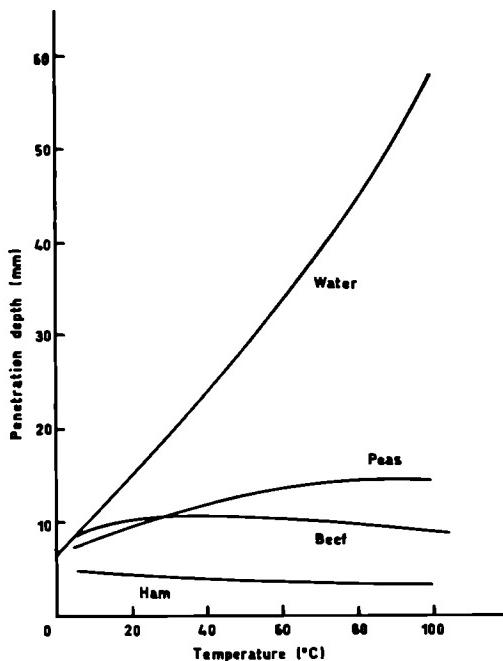


Fig. 2. Penetration depth for various foods at 2450 MHz (Ohlsson, 1983b).

develop in patterns that are difficult to predict. However, since the microwaves can be assumed to follow the laws of optics with reflections and refractions at interfaces between materials of different optical/dielectric properties, many of the peculiarities in microwave heating can be explained. An example is the concentration of the microwave field in the centre of spheres and cylinders (Ohlsson and Risman, 1978). The sphere acts as a microwave resonator, the microwaves entering the sphere being internally reflected, because of their very limited angle of incidence and the effect of laws of refraction. Corner and edge overheating effects can also to a large extent be explained by these phenomena (Ohlsson, 1983b).

The dielectric properties of the materials are needed both for the 'optical explanations' and for proper calculation of the microwave field distribution. Such calculations of centre heating effects in spheres have been the basis for the development of modified plating techniques in the food service industry (Ohlsson and Risman, 1978; Ohlsson and Thorsell, 1984).

Calculation of microwave field patterns in foods can be quite complicated if all dimensions and the variations in the amplitude, phase

and angle of inclination are to be considered. Quine (1980) and Bakanowski (1980) have presented calculations illustrating the relationship between the energy distribution in the food and the microwave field in the oven, created by the feed and antenna system. Such calculations have influenced the development of new microwave feed systems in modern microwave ovens.

MICROWAVE PROCESSING

For an analysis of the actual temperature distribution in microwave heated foods, the effects of heat conduction on the energy distribution created by the microwaves should be studied. Heat conduction has an important role in microwave heating, as already pointed out by Ohlsson and Bengtsson (1971), where the basic calculation method was also given. The calculation requires that the dielectric properties at different temperatures for the different foods be known. With the help of these calculations the influence of important variables such as frequency, power density and thickness has been studied for different industrial microwave heating processes.

Such calculations have been used both for analysing the proper process and product to select in development projects and for optimising existing microwave heating processes in the industry. The influence of the thickness, power level and power pulsing sequences on the uniformity of the heat penetration has been utilised for modelling the heating in domestic microwave ovens. As an example, the study showed that when using pulsed heating to reduce the average power level the heating pulses must be short, less than 10 s, to be effective in improving the heating uniformity (Ohlsson *et al.*, 1975). When modelling the microwave cooking of prebrowned meat patties, it was found that using microwave heating as a means to reduce the cooking time at high temperatures, where juice losses are great, was beneficial only for meat patties exceeding 10 mm in thickness (Ohlsson, 1976).

Microwave thawing has also been modelled as part of an industrial development project (Ohlsson, 1983a). This showed that, at 915 MHz, thick (>15 cm) blocks of foods can be thawed completely with very good temperature uniformity, if a thawing time of 8–10 h is acceptable.

Finally, dielectric properties of foods at sterilisation temperatures up to 140°C have been measured to serve as a basis for the Multitherm project for the microwave sterilisation of foods packed in plastic pouches. The process is based on the heating of the foods while immersed in water. The reason for this concept is that the dielectric properties of water are similar to those of

the foods, so that the microwaves will view the food and the surrounding water as one and the same dielectric material. Thus hot and cold spots at corners and edges caused by reflection and refraction at interfaces between foods and materials of very different dielectric properties, e.g. air, can be avoided. Further, the dielectric loss factor of water at high temperatures is low (see Fig. 2), so that little microwave energy is lost in heating the water. Dielectric measurements and modelling of the microwave heating process demonstrated that there are no benefits in using lower frequencies other than 2450 MHz. This was previously expected, as the wavelength in air and water is much longer at lower frequencies (Fig. 3) (Ohlsson and Bengtsson, 1975).

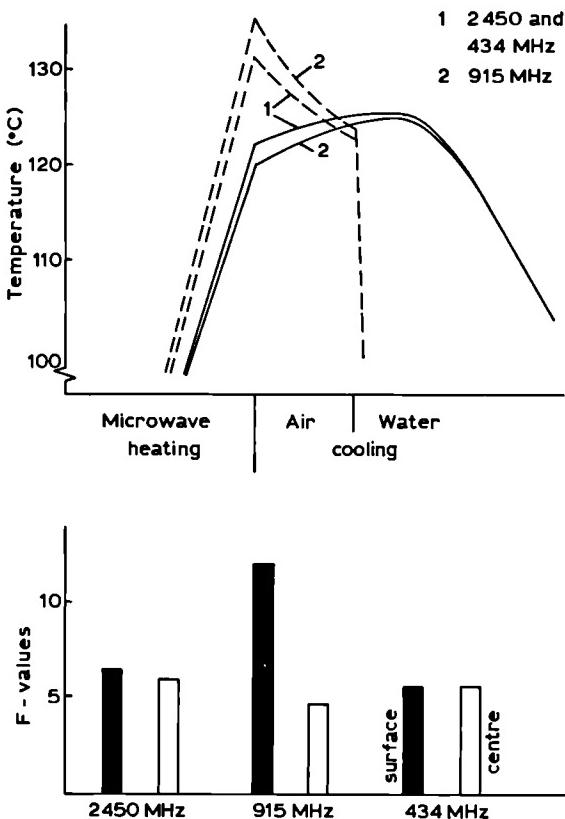


Fig. 3. Modelled microwave sterilisation of 20-mm slabs of beef at different frequencies, with a surface power density of 2 W cm^{-2} at both surfaces (Ohlsson and Bengtsson, 1975).

Recently, the modelling of the microwave heating process was used to determine processing variables such as power levels and water temperatures in the development of the first commercial installation of the Multitherm system in a Swedish food plant.

More data on the dielectric properties of plastics and other construction materials measured at the correct frequency and covering the temperature range of actual use are needed by the oven design and packaging industries. For foods, dielectric data covering a wider range of water contents are required, including data for bread and other semi-dry products. In addition, data are lacking on formulated foods. Measurements on such products might help to clarify the effect of different components and additives on the dielectric properties. Reliable prediction models for dielectric properties can be of great use when actual measured data are not available. Thus more universal models should be developed that can take many different components, additives and temperatures into consideration.

PROCESS CONTROL

Dielectric properties are very dependent on the amount of water in the material, so it is not surprising that dielectric measurements are used to determine the water content in materials. This method offers very rapid moisture determination without physical contact between the measuring head and the material. The power levels are low and the method is safe. In addition, only rotationally mobile water is measured, which is the water important to the stability of many food products. The presence of steam does not interfere as it does in many other methods.

There are quite a number of microwave moisture measuring systems in the paper and textile industry, but their use in the food industry is very limited. This may seem surprising, since there are many research reports on the high correlation between dielectric properties (or a measured value corresponding to them) and water content for foods of water content up to 20%.

Many different types of microwave moisture measuring sensors have been proposed. The most common ones are the open horn type and the resonator type (Fig. 4). Industrial equipment for measuring the water content in continuous production lines is available, using both these types of sensor. Laboratory equipment for determining the moisture content of batches of granular and powdered food products with up to 20% moisture content has been developed (Slight, 1970). The sensors are usually of the

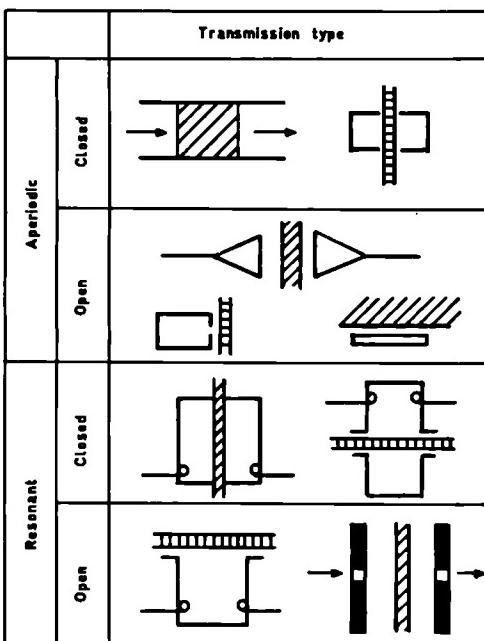


Fig. 4. Microwave moisture-measuring sensors (Kraszewski, 1980).

horn antenna type with a sample holder placed between the transmitting and receiving horn. In the equipment the power attenuation is measured and converted into moisture content. Since the attenuation, A , is predominantly due to the water it can be written (Kraszewski, 1980)

$$A = L \times (k_1 \times M_w/v + k_2 \times M_d/v)$$

where L is the thickness of the material; v is the volume; and M_w and M_d the masses of the water and dry material, respectively, k_1 and k_2 are constants.

The equation above indicates that the density and mass of the material will influence the measured value which is converted to water content. The sensitivity to density variations is a major drawback for this measuring method. This can be overcome, however, by measuring both phase and attenuation changes (Kraszewski, 1973; Kent and Meyer, 1982; Meyer and Schilz, 1980). The resonator methods are also sensitive to variations in distance between sample and sensor.

Another difficulty is that the relationship between the dielectric properties (or the attenuation) and the water content will vary for different

food materials because the strength of water binding may be different at low moisture contents. In different foods the amount of bound and free water will vary depending on composition and recipe. The chemical complexity of foods will mean that dielectric methods are not universal but must be calibrated for different foods.

However, for the same food or recipe high correlation between dielectric properties and water content has been found even for higher moisture contents (Ohlsson *et al.*, 1974).

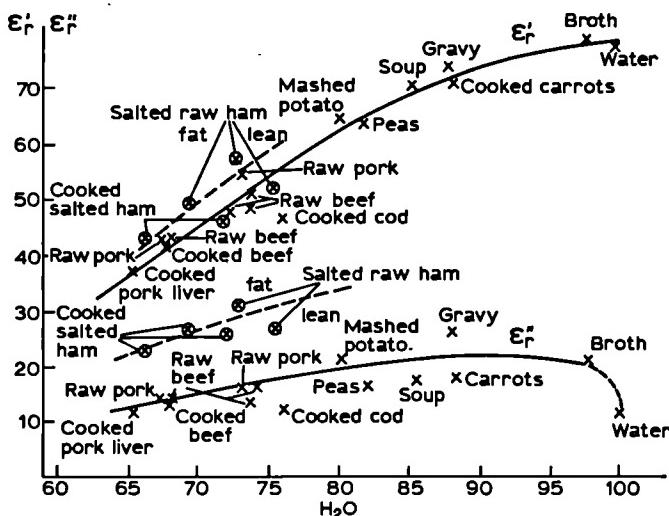


Fig. 5. The relationship between water content and dielectric properties for various foods at 2.8 GHz (Bengtsson and Risman, 1971).

Variations in sample temperature also markedly influence the measured value. This has become a problem for use in industry where the temperature of the processed foods to be measured varies during production.

For higher moisture contents, the relationship between dielectric constant and water content is no longer linear. As shown in Fig. 5, the dielectric loss is almost constant at high water contents. Further, the dielectric permittivity can have different values for different foods at the same water content, depending on the influence of the dissolved ions and other components on the polarity of the water molecules in the foods.

The high dielectric loss factor at high water contents imposes tight

restrictions on the sample sizes, otherwise the coupling between transmitted and measured signal will be too tight and the dynamic range too small. The resolution of the microwave moisture measuring method is often insufficient at high moisture contents.

Although much research has been done on microwave moisture measuring methods based on measuring the dielectric properties of food, the fact is today the most common microwave method to determine the moisture content in food samples is to simply dry the food in a microwave oven for a few minutes, replacing the standard drying oven which requires hours (Christie *et al.*, 1985). The reasons for the success of this method are, firstly, low cost; next, comparability with other established methods; and finally, probably less sensitivity to variations in the degree of binding of the water in the food.

The rapid automation of the food processing industry occurring today increases the need for sensors for measuring different important processing variables such as water content. Microwave moisture measuring methods offer many advantages, as stated above, but also some limitations in their present state. In the future, the measuring equipment must, for economic reasons, be more universal in its areas of application. With the development of solid-state electronics and computerised data processing a microwave method could be developed to overcome some of the above-mentioned limitations, but this would require that the influence of the limiting factors are better understood. For this more measurements are needed on the dielectric properties of foods to clarify the influence of important variables on the measured signals.

CONCLUSIONS

For both microwave heating applications and microwave moisture measurement, more data on the dielectric properties of foods are needed, both for a better understanding of the heating properties of different food materials and of the influence of different variables on microwave moisture measurements.

However, for extended industrial use of microwave applications (and by implication the need for dielectric properties), the food industry must see the economic benefits. There cannot be only technological push, there must also be market pull. There is also a clear need to develop the markets for both microwave heating and measuring applications by finding better economic solutions that can meet the needs of the food industry.

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DISCUSSION

R. E. Mudgett: In your high-temperature measurements, did you measure water alone and solids alone at 100°C? *T. Ohlsson:* Yes and no. Water alone and various foods, but not dry solids alone. *Mudgett:* Were there any discontinuities in the response of either the water or the foods above 100°C? Would you expect any in the solids? *Ohlsson:* No. The pattern was similar to those at low temperatures. *W. E. L. Spiess:* Microwave processing appears to require products to be designed specifically for it. *Ohlsson:* Yes. In addition to uniformity of heating, the product should be of good market—including organoleptic—appeal, and some of the more serious hazards of heating in microwave ovens should be avoided, such as sharp corners, difficult geometries, which lead to uneven heating. *E. Kress-Rogers:* Density differences usually show as perturbations in the microwave field and this includes bulk density differences. We have shown that microwave measurements can be used to determine simultaneously bulk density as well as moisture content in the case of powders, for example. Do you think this would be useful? *Ohlsson:* Yes, not only water content can be determined by electrical measurements, but other properties also.

H. Schubert asked how uniform was the temperature in short-time microwave sterilisation of foods. *Ohlsson* confirmed that completeness of sterilisation was and must be a primary requirement of such processes. Temperature uniformity had been confirmed experimentally but they had gone further and had used inoculated packs to check for sterility—which was confirmed also. The commercial operation would also use such inoculated packs regularly as routine to confirm that sterility was maintained. Temperature distribution measurements were useful but not enough. Most important was commercial sterility. *Schubert:* How did you measure temperature distributions? It is also important to avoid local overheating. *Ohlsson:* Certainly. Thermocouples were inserted into random packs immediately after processing, destructively. In-process temperature measurement would be extremely difficult. *Kress-Rogers:* Your results showed the effect of protein and fat content in meat emulsions. Could this offer a method for determining such components? *Ohlsson* thought that that would only be possible when a particular emulsion had been 'calibrated' in advance, by subtracting the water content effect. That might be too expensive a method for commercial use.

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Microwave Properties of Some Food Liquids

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The complex dielectric constants $\epsilon = \epsilon' - j\epsilon''$ of salad cream and some sugar solutions were measured at 3 GHz as functions of temperature.

The entities ϵ' and ϵ'' were determined by a cavity perturbation method. Standing wave ratio d at resonance and change of resonance frequency $\Delta\nu$ induced by the samples were measured. For the empty cavity, $d = 1$ (see Fig. 1).

From d and $\Delta\nu$:

$$\epsilon' = C_1 \Delta\nu + 1 \quad \epsilon'' = C_2(d - 1)$$

where the constants C_1 and C_2 are determined by calibration with water of known ϵ' and ϵ'' .

A. Salad Cream (See Fig. 2 and Appendix for details)

Dielectric constants for emulsions from Londreco Ltd, were measured at temperatures from -90°C to $+90^\circ\text{C}$, for different droplet sizes and storage temperatures. The effect of droplet size was not significant, possibly due to a rather broad size distribution in each emulsion.

At about -15°C , a very steep reduction in ϵ' and ϵ'' was seen for cool-stored samples. Recycling the temperature variation around the transition temperature did not induce changes of the temperature dependence (hysteresis).

For all samples, the ϵ curves changed considerably on extended storage at room temperature.

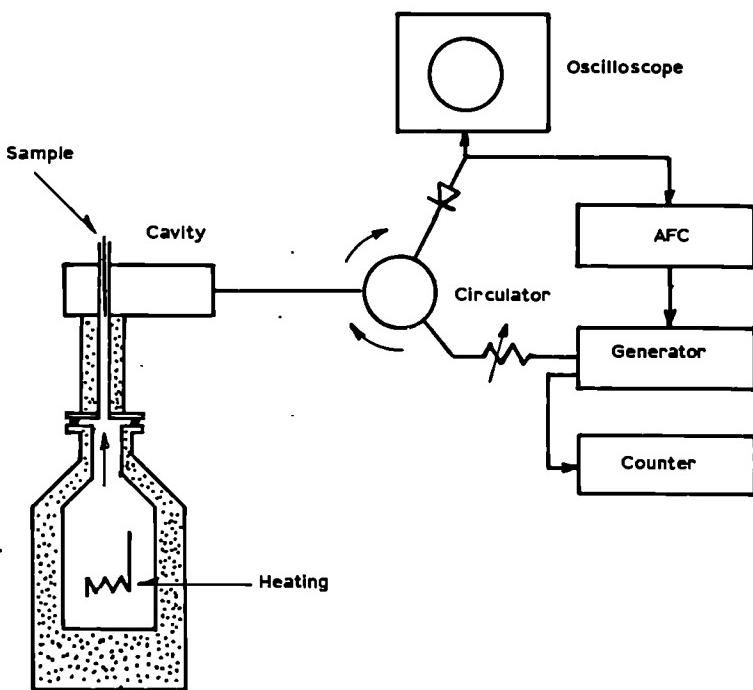


Fig. 1. Equipment for measuring the dielectric constant of liquids at 3 GHz, from -90°C to $+20^{\circ}\text{C}$.

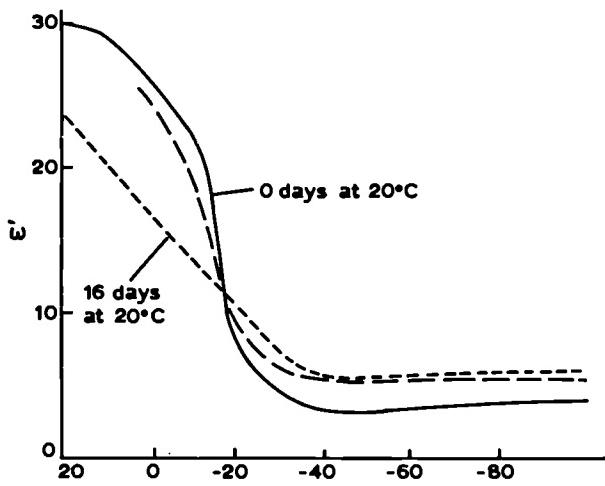


Fig. 2.

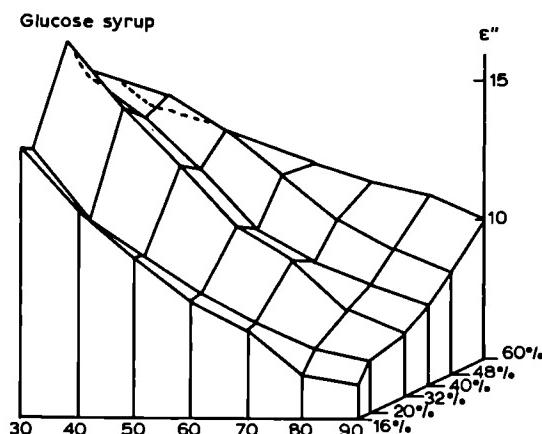
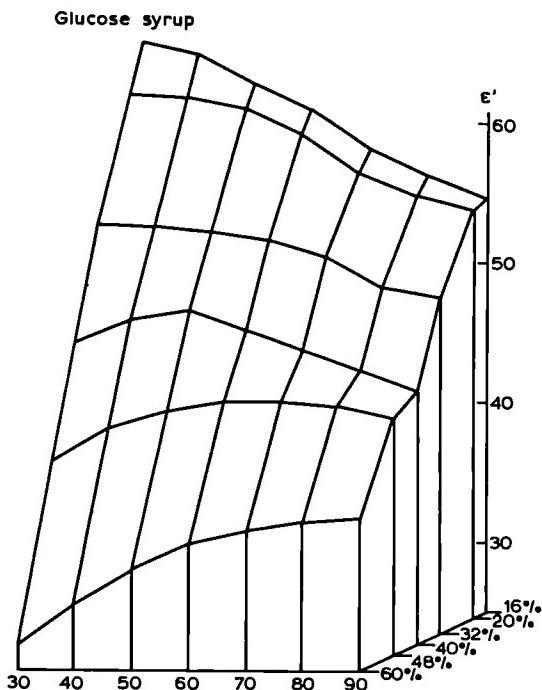


Fig. 3.

B. Sugars (See Fig. 3)

Dielectric constants for different concentrations of sucrose, dextrose and glucose syrup were measured from +30°C to +90°C. For all the main constituents, over the whole temperature range, ϵ' was seen to decrease with increasing concentration of the solutions. At 30°C, ϵ'' reached its maximum value at a concentration of 40%. At higher temperatures, this maximum shifted to higher concentrations. These findings are in accordance with the results presented by M. Kent and E. Kress-Rogers (Chapter 14).

APPENDIX

TABLE A1
RECIPE FOR SALAD CREAM SAMPLES

<i>Substance</i>	<i>Composition by weight (%)</i>
Water	30·2
Malt vinegar (8·5% acetic acid)	18·7
80% acetic acid	0·27
Vegetable oil (sunflower)	27·0
Sucrose	15·8
Salt	2·4
Egg yolk	4·93
Vegetable gum (carob bean)	0·7

Three samples of mean droplet diameter 2·20, 2·72 and 3·75 μm were prepared and distributed.

Measurement of the Complex Permittivity of Dielectrics during Microwave Heating: Study of Flours and Starches

MAUD SERAS, BEATRICE COURTOIS,
SOPHIE QUINQUENET and MICHEL OLLIVON

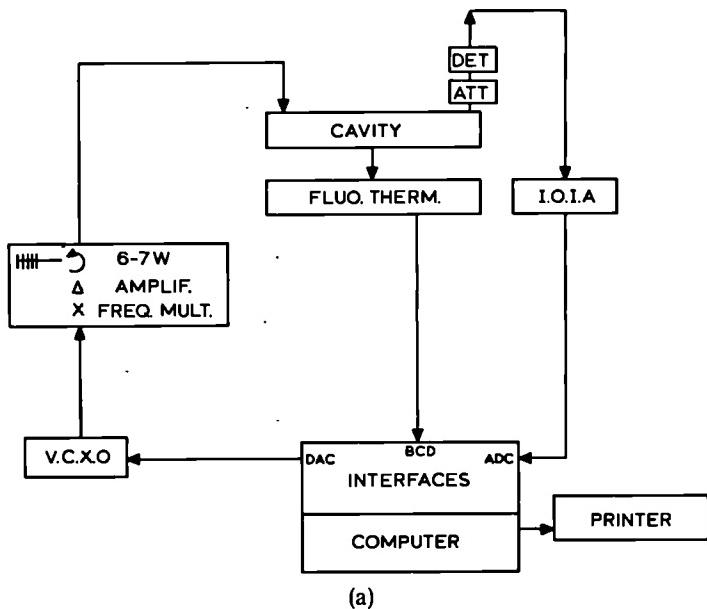
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INTRODUCTION

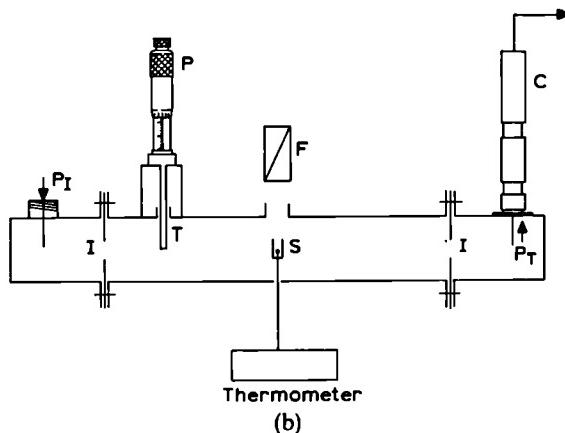
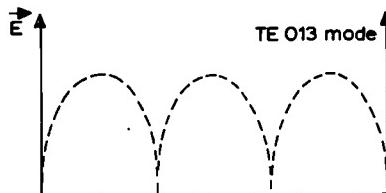
The water content and its interactions with the matrix of a food product are useful for industrial applications since the mobility of water is involved in texture and preservation, as well as for fundamental research. On the other hand, the unique properties of microwave dielectric heating are more and more used in the food industry for processes such as drying, cooking or sterilisation and lead to a need for data on microwave dielectric properties. For this purpose a method has been developed to measure complex permittivity of samples as a function of temperature during microwave heating. These permittivities have been related to water content and interactions. Water content has been varied on eight different flours. Four starches were also examined. Only the general behaviour which has been deduced for both flours and starches will be discussed here.

METHOD AND RESULTS

A simple, fast and fully automated method for measurement of complex permittivity and temperature of flours and starches samples heated by microwave adsorption at 2·43 GHz, using the small perturbation technique, was chosen (IEEE-MTS-S Int. Symposium, St Louis, June 1985, p. 645). In this system, a microcomputer continuously monitors a resonant cavity containing the sample via a frequency-controlled generator, in a closed loop circuit (Fig. 1a). The sample positioned at one of the electric field



(a)



(b)

Fig. 1. (a) Closed loop circuit monitoring the resonant cavity. (b) Sample S in the resonant cavity.

maxima (Fig. 1b) perturbs the cavity resonance. The perturbations are compared to standards (e.g. decanol) to determine the dielectric constants ϵ' and ϵ'' of the product. Temperature is measured inside the sample by a nonperturbing fluorimetric thermometer, with an optical fibre as temperature probe which is a close fit with the sample holder (made of Teflon with a very thin wall between the fibre and the sample).

Sample temperature and both dielectric constants are recorded as a function of time (Fig. 2a). From these data, dielectric constants are plotted as a function of temperature (Fig. 2b). All flours, including wheat, corn, rice, even potato, behave similarly.

Wheat flour samples of water contents from 3 to 10% were obtained by dehydration at 60°C. Figures 3a, 3b and 3c show the superposition of the curves of temperature, ϵ' and ϵ'' as a function of time for these samples.

It appears, first, that under microwave irradiation, flour samples dry in a few minutes to a moisture content less than 0.3% regardless of the initial water content. Second, that for a given temperature ($T = 30^\circ\text{C}$), despite variations due to water, granulation and packing, wheat flour dielectric constants are found to vary linearly with water content W (Fig. 4).

Heating Kinetics

For all the samples the heating curve is the same. Below 100°C evaporation increases with temperature but water losses do not exceed 10% of the initial water content. Thus, microwave energy is mainly directed to heating the sample, so that the temperature rises very rapidly. Then there is a slight temperature increase domain corresponding to water evaporation. Finally, the temperature plateau was attributed to an equilibrium between a reduced energy absorption and thermal losses from the sample.

Dielectric Permittivity as a Function of Time

In each case three phases are observed:

Phase I: Heating of the product

The increase of ϵ' before 100°C found for both the dry and the 10% water content product shows that the water is in interaction with the polysaccharide matrix. Confirmation is given by DSC measurements which confirm that the water is unfreezable. Both water and polysaccharide polar groups (mainly hydroxyl) contribute to the permittivity values, as long as the temperature is below 100°C, which assumes that water molecules are far enough apart not to interact with each other.

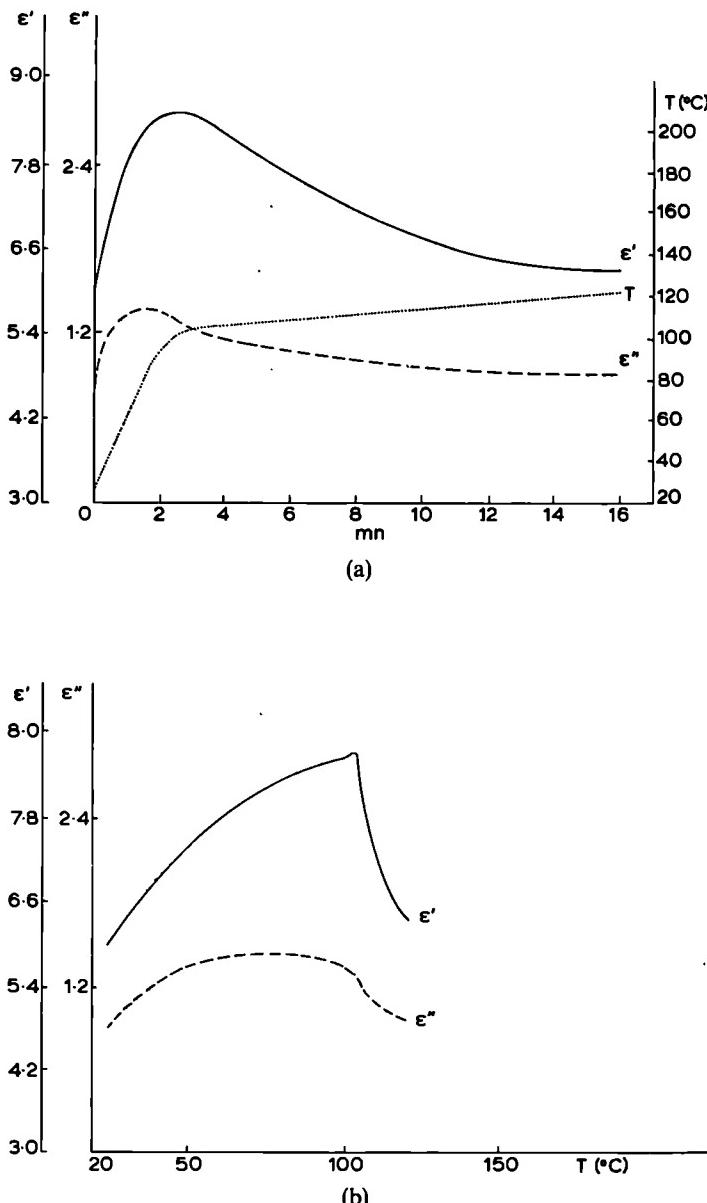


Fig. 2. (a) Heating kinetics and permittivity changes for a wheat flour sample.
 (b) Dielectric constants of a wheat flour sample versus temperature.

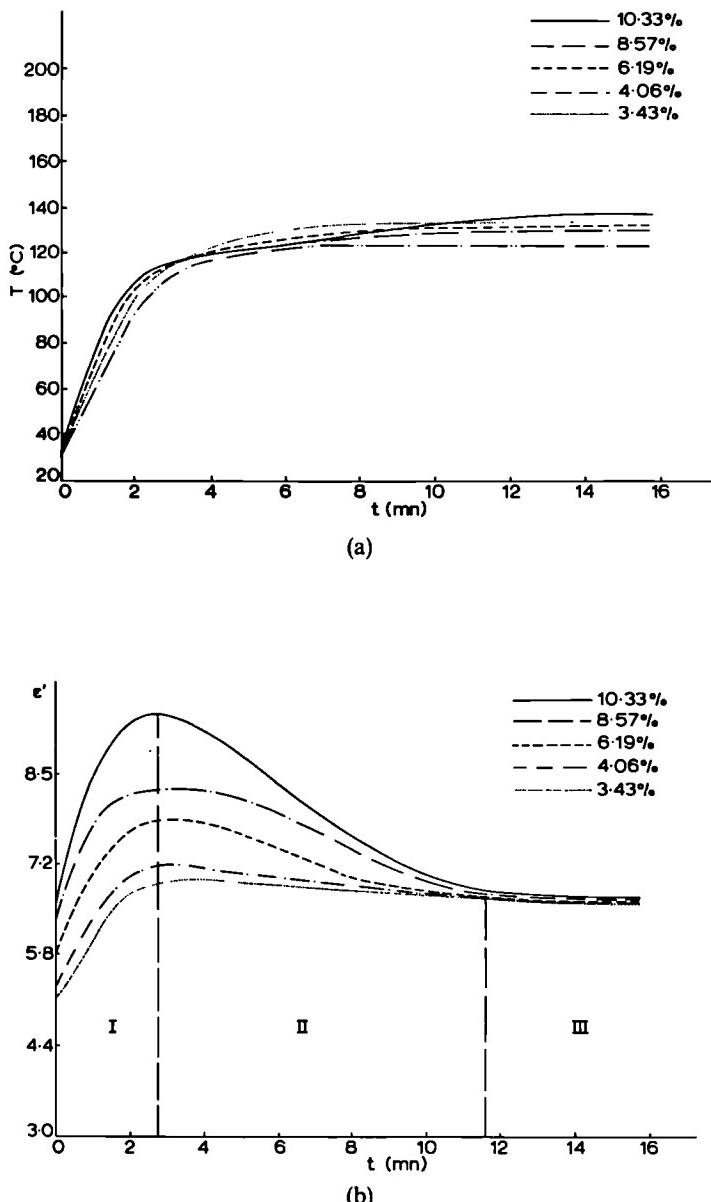
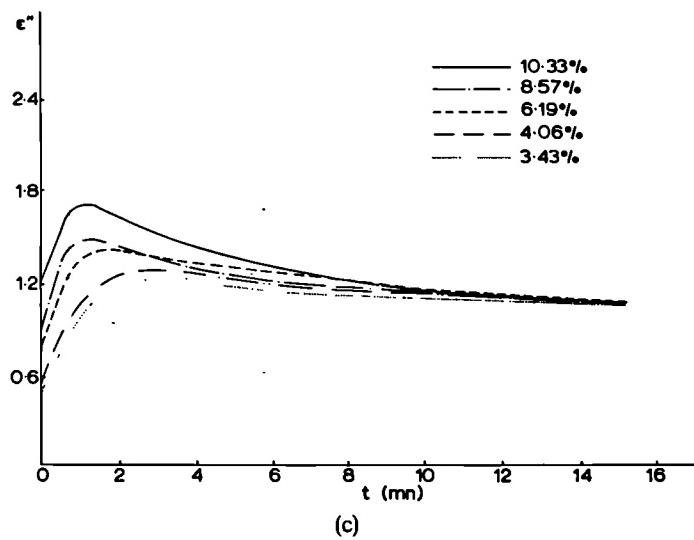
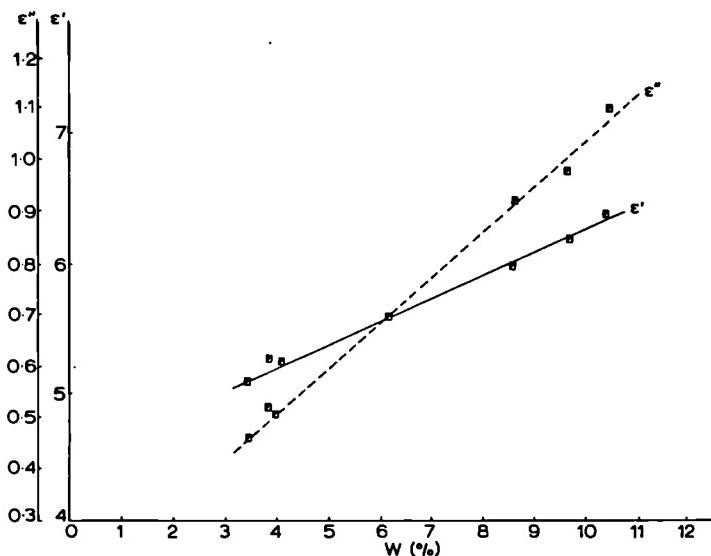


Fig. 3. (a) Heating kinetics of hydrated wheat flour samples. (b) Permittivities of hydrated wheat flour samples. (c) Losses of hydrated wheat flour samples.



(c)

Fig. 3.—*contd.*Fig. 4. Dielectric constants ϵ' and ϵ'' at 30°C versus water content.

Phase II: Evaporation of water
 ϵ' decreases because of water loss.

Phase III: The dry product

The stabilisation of ϵ' at the end of the experiment corresponds to the final temperature plateau: the equilibrium state of the dry product is reached.

Dielectric losses as a function of time

The dielectric losses show the molecular relaxation phenomena. When water evaporation occurs, ϵ'' decreases to reach a plateau equivalent to the ϵ'' of the dry product. At 80°C there is a maximum relaxation for the type of water considered corresponding to a maximum of ϵ'' . The maximum temperature depends on the water-matrix interactions.

CONCLUSIONS

The water content is an important characteristic of most food products for reasons of texture as well as for stability during storage. Depending on its proportion, the temperature and the food constituents, water interacts differently with the matrix. So, water interactions are as important as water content and the method described allows both to be seen. Microwave permittivity and loss measurements and the relaxation maximum found at 80°C indicate that water in the 3–10% range is not tightly bound to starches.

Microwave heating and drying is developing very rapidly in industrial food processing. This method allows investigation of the food behaviour from simple heating to complex reaction, including drying as illustrated above, under microwave irradiation and heating.

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Dielectric Properties of Dairy Spreads

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INTRODUCTION

In recent years, consumption of butter in Ireland has been falling, due mainly to two factors: (1) the poor spreadability of butter at refrigeration temperatures and (2) concern about the health aspect of butterfat. The Irish Dairy Industry's response to this has been to introduce a range of low fat, high moisture spreads and a range of spreads containing soya oil which changes the fatty acid profile, thus increasing spreadability. This project is concerned with measuring moisture dispersion and its effects on dielectric properties. Traditional ways of measuring moisture dispersion have been to use indicator paper which changes colour on contact with water. This picks up droplets on a freshly cut surface. The second method is to prepare a thin slice of the spread and view under a microscope. This is useful in that size as well as number of droplets can be measured. However, slide preparation is difficult and distortion of droplets may occur. Dielectric measurement is most useful in that it is applicable to continuous production. The difficulty lies in proper calibration of instruments and lack of information on the effects of vegetable fats on dielectric properties.

METHOD AND MATERIALS

The permittivity jig is designed for three-terminal measurements of the permittivities and loss factors of solid materials. Sample discs, 0.2 in thick are prepared with aluminium discs on either side. These are tested at 4°C. The system used allows control within $\pm 1^\circ\text{C}$. The frequency range used is 0.1-4 MHz. Care is taken not to compress the samples in the jig as this

TABLE 1

Spread	Composition		
	Water (% w/w)	Salt (% w/w)	Kind of fat
		Milk fat	Soya oil
Dairygold	23.0	1.73	✓
Easigold	26.0	1.80	✓
Goldnsoft	22.0	1.75	✓
Lough Egish	15.5	2.00	✗

affects the readings. A weight of 50 g is used to maintain uniform pressure on the samples. Samples are stored in a refrigerator at 4°C before testing. The specific materials examined are listed in Table 1.

RESULTS

For results see Figs 1 and 2.

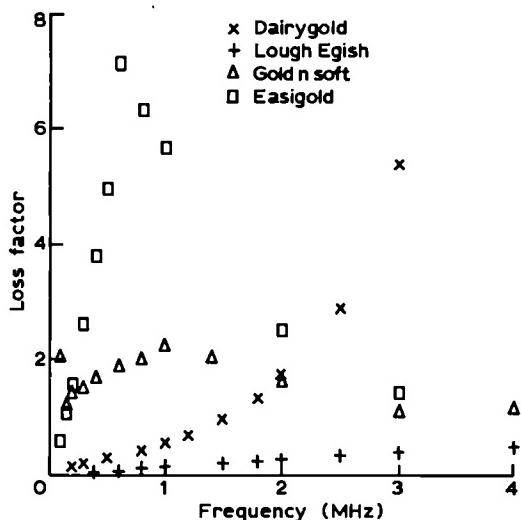


Fig. 1.

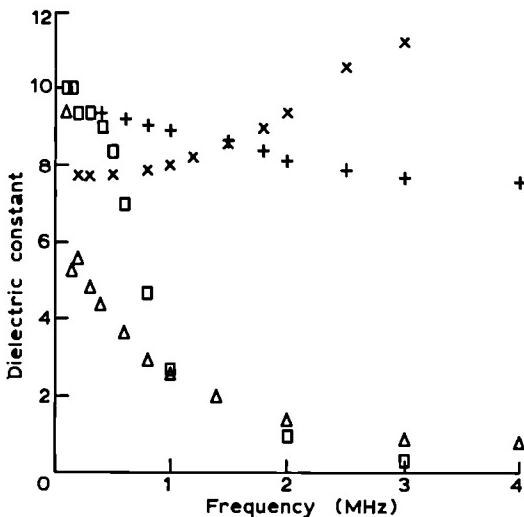


Fig. 2.

CONCLUSIONS

The indicator paper proved inefficient due to the small size and degree of dispersion of the droplets. Microscopic examination was useful but examination of spreads of high moisture content was difficult due to distortion of droplets. Photographs were difficult to take due to the small refractive index difference between the water and fat. Dielectric analysis is easily done but the main problem is with calibration. Future research will concern itself with trying to correlate the properties of laboratory-made spreads of known composition with commercially-made spreads. In this way more knowledge of the effects of moisture dispersion on dielectric properties can be obtained.

Dielectric Study of Food Emulsions at Subzero Temperatures by the Thermally Stimulated Depolarisation (TSD) Technique

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This report is on the dielectric behaviour of three salad cream samples having the same composition but different mean droplet diameters, and of a simpler water-in-oil emulsion with approximately the same water content as the salad cream samples, by means of the thermally stimulated depolarisation (TSD) technique in the temperature range of 77–300 K, in an attempt to contribute to a better understanding of the physical properties of food emulsions and their dependence on the characteristics of the emulsions. There is particular interest in whether the dielectric behaviour of salad cream samples depends on droplet size or not, whether the characteristics of the dielectric relaxation of water molecules in the salad cream samples and the simple emulsion are the same or different and if the greater complexity (and particularly the higher conductivity) of the salad cream samples compared to the simpler emulsion manifests itself. The TSD technique¹ is especially suitable for such studies, since it is spectroscopic, it is very sensitive to low concentrations of dipoles and it offers the possibility to resolve experimentally relaxation processes arising from sets of dipoles with slightly different relaxation times.

The salad cream samples were prepared by Londreco (England), (see Chapter 16 for details). Their water content was about 53% and their mean droplet diameter 2.20, 2.72 and 3.45 μm . The simpler water-in-oil emulsions were prepared by l'Oreal (France). Their water content was 50% and their mean droplet diameter about 2 μm .

The TSD plots of the salad cream samples show three peaks at 135 ± 2 , 190 ± 3 and 204 ± 2 K independently of mean droplet diameter. The activation energy of the low-temperature peak at 135 K is also independent of droplet diameter and equal to 0.30 ± 0.02 eV. The TSD plots of the

simpler water-in-oil emulsions show two peaks at 134 ± 2 and 227 ± 2 K. The activation energy of the low-temperature peak is 0.28 ± 0.02 eV. Finally, TSD plots obtained with macroscopic polycrystalline pure ice show two peaks at 119 ± 2 K (with an activation energy of 0.25 ± 0.01 eV) and 220 ± 2 K.

The first conclusion which can be drawn from these results is that the salad cream samples show quite identical dielectric behaviour independently of their different droplet sizes in the range studied. Measurements performed at SIK Goteborg (Sweden) at 2.8 GHz and at 10, 20 and 30°C and at the Electrophysics Department, Technical University of Denmark at 3.05 GHz in the temperature range -90 to +20°C under the COST 90bis collaboration support this conclusion.

The low-temperature TSD peaks of macroscopic polycrystalline pure ice at 119 K and of the simpler water-in-oil emulsions at 134 K have been attributed to reorientation of water molecules.^{2,3} Several indications support the conclusion that the low temperature TSD peak of the salad cream samples at 135 K has also to be attributed to reorientation of water molecules in the ice microcrystals. The results show that, regarding this relaxation of water molecules, the salad cream samples and the simpler water-in-oil emulsions show quite identical behaviour. They show, further, that this relaxation is slower in the salad cream samples and the simpler water-in-oil emulsions than in macroscopic polycrystalline pure ice, for reasons which can well be understood.³

It is consistent with these results that at temperatures above about 160 K the dielectric behaviour of the salad cream samples is quite different from that of the simpler water-in-oil emulsions, i.e. regarding the dipolar relaxation of molecules larger than water molecules and the space charge relaxation the two systems show quite different behaviour from each other. In fact, by studying the dependence of the position and the magnitude of the peaks at 190 and 240 K on the polarisation conditions, it can be shown that the first peak is probably of dipolar origin and the second peak of space charge origin.

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A Dielectric Study of the Binding Modes of Water in Mono- and Disaccharides

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This report is on a dielectric study of frozen aqueous solutions of the monosaccharides glucose, mannose, galactose, ribose and arabinose and the disaccharides cellobiose, lactose and maltose in the temperature range 77–270 K and over a wide range of concentrations, $c = 0\text{--}0.0003\text{--}1.5 \text{ mol/litre}$, and of hydrated compressed pellets of galactose and maltose in the temperature range 77–300 K and at different water contents, $h = 0.9\text{--}20.8\%$, by means of the thermally stimulated depolarisation (TSD) technique. Of interest are the hydration properties of the saccharides, i.e. the fraction of water influenced by the saccharide molecules (hydration or bound water), the fraction of non-influenced water (free or bulk water), the hydration sites and the hydration mechanism.

The TSD technique consists of studying the thermally-activated release of stored dielectric polarisation.¹ The technique is characterised by the ability to resolve experimentally relaxation processes arising from sets of dipoles with slightly different relaxation times.

The TSD plots of the solutions show a band at 110–140 K and a peak at about 230 K. The low-temperature band at 110–140 K was studied in detail. Several indications support the hypothesis that it is due to reorientation of both free and bound water molecules. Regarding the shape of the band, the saccharides studied can be subdivided into two classes.

In the solutions of the monosaccharides glucose, mannose and galactose the band consists of a peak. In dilute solutions with c up to about 0.7 mol/litre the peak is multiple and the corresponding relaxation process continuously distributed, with both the activation energy W and the pre-exponential factor τ_0 in the Arrhenius equation being distributed parameters; in solutions with higher concentrations, on the other hand, the peak is approximately single. In the solutions of ribose, arabinose,

cellobiose, lactose and maltose, on the other hand, the band consists of two peaks numbered I and II in order of increasing temperature. The temperature T_M and the activation energy W of peak I are independent of solute nature and concentration and very close to those of the low-temperature TSD peak for pure ice. The relative contributions of peaks I and II to the magnitude of the band depend on solute and concentration.

The results for the solutions can be interpreted as follows. In the glucose, mannose and galactose solutions there is a continuous transition from hydration to free water molecules in dilute solutions with c up to about 0.7 mol/litre and only hydration water molecules in more concentrated solutions. In the solutions of the other saccharides there are two discrete kinds of water molecules, namely free and hydration molecules (peaks I and II respectively). These results can be discussed on the basis of the specific hydration model.^{2,3} Glucose, mannose and galactose are compatible with the ice structure, while the saccharides of the second class cannot fit well into the ice structure and thus act as structure breakers.

The TSD plots of the hydrated compressed pellets show a broad low-temperature peak at about 140 K and a complex high-temperature band. The low-temperature peak was studied in detail. It appears only when the water content h is higher than a critical water content h_c ; $h_c \approx 8\%$ for galactose and 4% for maltose. h_c corresponds to about 0.8 water molecules per saccharide molecule. The magnitude of the peak increases linearly with increasing h . The peak is multiple, the mean values of T_M and W being in good agreement with those in solutions and higher than those of the ice peak.

The results obtained with the compressed pellets can be interpreted as follows: all the sorbed water molecules up to a water content corresponding to $Z_h \approx 0.8$ water molecules per saccharide molecule are tightly (irrotationally) bound. This is the first time that the hydration number Z_h has been determined for compressed pellets of mono- and disaccharides. Consideration of the crystal structure of galactose and maltose makes reasonable the view that in both crystals probably only one oxygen atom per molecule is accessible to water, in agreement with this experimental result of $Z_h = 0.8$. All the sorbed water molecules in excess of 0.8 per saccharide molecule are loosely bound. They are thought to cluster around the tightly bound water molecules. The reorientation of the loosely bound water molecules is characterised by a continuous distribution of relaxation times, as a result of either a distribution of the number of hydrogen bonds formed by the water molecules in the clusters or a distribution of cluster sizes.

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Part 3

OPTICAL PROPERTIES

21

Food Colorimetry: Measurement and Interpretation

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SUMMARY

Measurement of the colour of foods can be by visual systems, tristimulus colorimetry, spectrophotometry, and specialised instrumentation for particular commodities. Visual systems involve comparisons with coloured references under controlled illumination. The tristimulus instruments employ three glass filters corresponding to the response of the cones in the human eye. The spectrophotometric method involves determining a reflection or a transmission spectrum. The fourth approach involves a wide range of specialised instrumentation designed to measure the appearance of particular commodities.

Recent trends in instrumentation are towards instruments to produce a reflection or transmission spectrum which can be used to generate tristimulus data, specific wavelength absorption data, colour differences, colour tolerances and readouts in terms of any desired reference colour solid. The introduction of micro-electronics has made this possible in a single instrument. It is now feasible to incorporate microcircuits which calculate almost any 'appearance' quantity but all depend on classic absorption or transmission spectra.

INTRODUCTION

To a newcomer interested in colorimetry of foods it will be immediately obvious that there is a bewildering array of approaches. They can be classified into roughly four categories: visual systems, tristimulus colorimetry, spectrophotometry and specialised approaches for different

commodities. This contribution is concerned primarily with tristimulus colorimetry and spectrophotometry.

THE DEVELOPMENT OF A TRISTIMULUS COLORIMETER

A colorimeter is an instrument designed to produce a readout that duplicates the response of the human eye. The human eye is a superbly sensitive organ and some engineers have complained that it presents unfair competition. Be that as it may, the response of the eye has to be understood in the design of an instrument. A great deal of research has been devoted to the physiology of vision and it is relatively well understood. Given appropriate input from the human eye, the brain is capable of making excellent judgements of colour. But it is easy to trick the eye by providing false or inadequate inputs. Modern instruments are carefully designed to provide adequate input.

A tristimulus colorimeter is a very simple instrument. All it needs is a light source, three filters which duplicate the response of the human eye, and a detector system (Fig. 1). The three filters correspond to the three primary colours (red, green, blue), the components of white light, which can be recombined to match any given colour. This arrangement (Fig. 2) can match most colours. The RGB sources can be produced physically in the laboratory but are inefficient in matching colours because not all colours can be matched directly. This can be remedied by choosing sources which will encompass all colours (Fig. 3). These sources are imaginary but, mathematically, very useful (Wright, 1969).

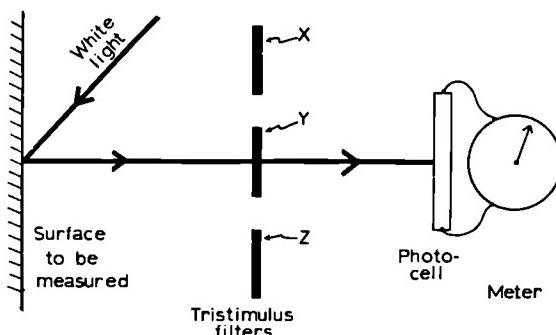


Fig. 1. A simple tristimulus colorimeter.

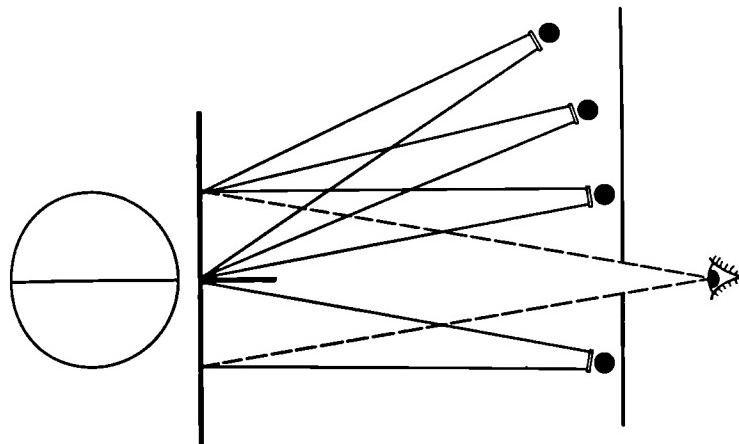


Fig. 2. Diagram illustrating the use of three primary colour sources (Red, Green, Blue) to match a given colour.

The eye has four types of receptors; rods sensitive to black and white and three types of cones sensitive to red, green and blue light respectively. The cones have recently been photographed in the retina and the genes responsible for each receptor pigment located (Nathans *et al.*, 1986). A panel can match the spectrum colours using the RGB sources and the data can be recalculated in terms of XYZ to produce the curves shown in Fig. 4. Then, in order to duplicate the response of the eye, all that is required is to produce glass filters with transmission curves duplicating the response of the human eye. A number of commercial instruments employ this principle.

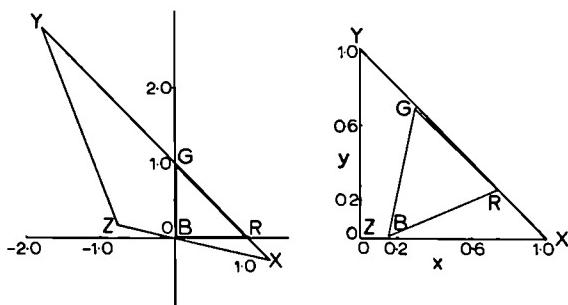


Fig. 3. The RGB solid superimposed on the XYZ solid.

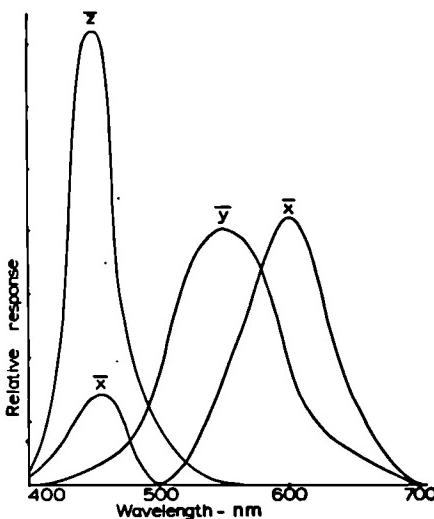


Fig. 4. Response of the human eye to the spectrum colours.

A SPECTROPHOTOMETRIC APPROACH

The response of the human eye was standardised in 1931 and led to what is known as the CIE system (Commission Internationale d'Eclairage) which was rapidly adopted world-wide. It was shown that when the response curves of the eye were known, any transmission or reflection curve could be transformed into CIE XYZ coordinates by the following equations.

$$X = \int_{380}^{750} RE\bar{x} d\lambda \quad Y = \int_{380}^{750} RE\bar{y} d\lambda \quad Z = \int_{380}^{750} RE\bar{z} d\lambda$$

The integral between 380 and 750 nm covers the wavelengths of the visual spectrum. R is a function of wavelength (λ) representing the reflectance or transmittance of the sample. E is a function of wavelength representing the energy distribution of the standard light source.

In earlier years, the point-by-point integrations were made manually and then graphically but this was too laborious. Mechanical and then electronic integrators were introduced but they were very expensive. Recently, however, the introduction of microelectronic circuitry in computers has greatly reduced the cost of integration. As the tristimulus colorimeters were developed to replace the laborious integration and to reduce the cost of

obtaining data, there has recently been a resurgence of the use of spectrophotometers for colour measurement and many instruments today have both spectrophotometric and tristimulus colorimetry readouts.

THE INTERPRETATION OF DATA

Colour measurement by either the tristimulus or spectrophotometric approach requires a light source. It is obvious that the energy distribution of the light on the sample will change the reflection curve. This can be handled easily in an instrument by standardising the energy source, but consumers may see the samples differently under different light sources. For example, tomato juice looks quite different under tungsten light and under fluorescent light: more spectacular effects are achieved by back-lighting. This is an important consideration when attempting to correlate instrument readings with consumer judgements.

The objective 'measure the colour of a sample' means 'locate the coordinates in colour space which represent that particular sample'. Many colour solids have been developed to encompass the range of colours discernible to the human eye. Two are possibly better known than the others. They are the CIE XYZ solid and the Judd-Hunter $L\ a\ b$ solid. Figure 5 shows the coordinate system of the $L\ a\ b$ solid. It was originally developed

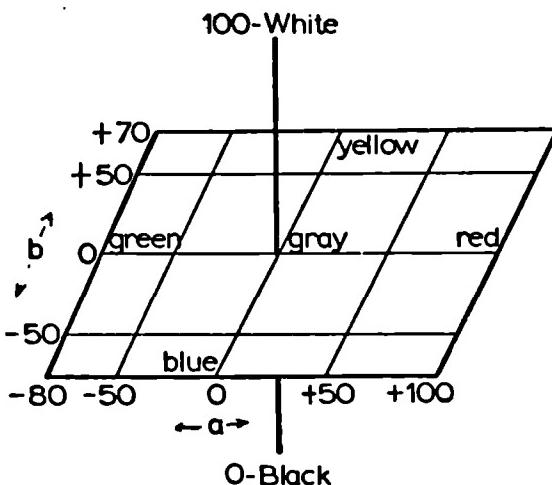


Fig. 5. The Judd-Hunter colour solid.

with two major objectives. One was to reflect the red-green and blue-yellow paired responses of the human brain and the other was that its system of units would provide equal visual responses in all portions of the solid. It is impossible to make a three-dimensional solid with equal visual responses in all portions of the solid but the *Lab* solid is close. Furthermore, the colour is easy to express in a conventional algebraic format. Results can be expressed in the *Lab* coordinates directly but in quality control applications, three-dimensions are inconvenient. Consequently, methods of reducing three terms to one or two have been developed. One popular transformation is to reduce the two *a* and *b* figures to a single one by calculating θ , the angle between a line joining a point (*a*, *b*) in Hunter space with the origin, and the green/red axis. It is actually a function of hue in which 0° would represent a red and $90, 180$ and 270° would be yellow, green and blue respectively. A colour can then be represented by *L* (lightness or darkness) and θ , a measure of hue. Both are easy to visualise and are independent of each other. This consideration is important if statistical analysis of variance is to be made on the data. The *Lab* quantities are not independent of each other which is a requirement for analysis of variance so *Lab* data analyses should be interpreted with caution.

Data in the *XYZ* system require a different interpretation since there is

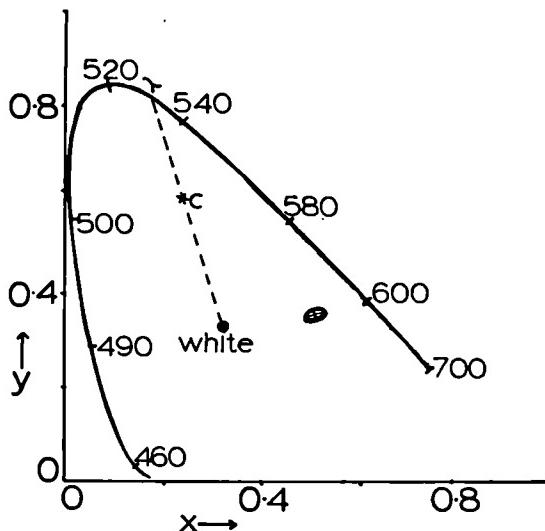


Fig. 6. Tristimulus values *x*, *y* with the locus of the spectrum colours.

no quantity in it comparable with θ . XYZ data can be used without transformation but it is difficult to visualise the colour and the units are non-uniform. One popular transformation is to change the data to tristimulus coefficients by the following equations:

$$x = \frac{X}{X+Y+Z} \quad y = \frac{Y}{X+Y+Z} \quad z = \frac{Z}{X+Y+Z}$$

The x, y data can be plotted in familiar graphical form as shown in Fig. 6. The colours of the spectrum plotted in this way allow visualisation of the colour. Every colour can be represented by Y which relates to lightness/darkness, and x, y related to hue and chroma as used in the nomenclature of the Munsell visual colour solid. Note that \bar{x}, \bar{y} and \bar{z} as used in the integration of the spectrophotometric curve are merely special cases of tristimulus coefficients. The x, y system is used in many industries particularly those involving light sources.

COMPARISONS OF DATA

Tristimulus data obtained from completely opaque or perfectly transmitting samples is theoretically accurate in terms of the CIE standardisation of the human observer. Unfortunately, few samples, particularly foods, fit these absolute criteria. Most reflecting samples also absorb some light and most transmitting samples scatter and reflect some light. Some samples may be equally reflecting and transmitting. Conventional approaches to measuring samples which obviously transmit some light are to measure by reflection using a cell filled with sufficient sample that greater depth of sample does not change the reading. Obviously this introduces some arbitrariness into the readings with its obvious implications for correlation with visual judgements.

In order to decide whether a sample should be measured by reflection or transmission, the Kubelka–Munk theory can be used. This colorant layer concept has been used extensively in paint, textile and plastics applications to determine pigment mixtures. It assumes that the optical properties of the material can be described accurately at each wavelength by a scattering coefficient S and an absorption coefficient K , using the equation

$$K/S = kC$$

where K = the light absorbed, S = the light scattered, C = concentration of

colorant and $k = \text{a constant}$. The ratio K/S is related to reflectance at a given wavelength by

$$K/S = \frac{(1 - R)^2}{2R}$$

where R = reflectance of an infinitely thick sample. The values of K and S can be calculated separately and used to decide the mode of measurement. Samples with a high value of K and low value for S should be measured by transmission and vice versa. The Kubelka-Munk applications have been described in detail by Judd and Wyszecki (1963). Tristimulus data can be used in place of reflection data in the Kubelka-Munk equations and this results in some improvement in correlations with visual judgements but the increase in accuracy may not be worth the extra computation effort (Francis and Clydesdale, 1975).

Another problem in comparison of data is the use of instruments of different designs. The geometry of sample presentation is usually different and this results in differences in absorption and scattering. The problem is further compounded by the use of different colour solids with different instruments. The mathematical equations for interconversion of data from one colour solid to another are not perfect. In earlier years, assumptions made for the proposed simplification led to errors but this situation is improving. Modern computer equipment can handle much more complicated equations with corresponding increases in accuracy.

- A less serious problem in data comparison is the use of a number of instruments of the same design. Presumably they were all calibrated against a master tile by the manufacturer and can be calibrated against each other by circulation of calibration standards. Such intercalibration used to be a more serious problem but today the instruments are more stable and more alike in performance.

RELATIONSHIP BETWEEN COLOUR AND PIGMENT CONTENT

The measurement of colour for quality control and/or consumer acceptance is worthwhile in itself but it is possible to broaden the concept. The tristimulus colour readings can be related to pigment concentration. Figure 7 shows the relationship between Lab readings and the concentration of cyanidin-3-glucoside (Cn-3-G), a common red anthocyanin pigment found in fruits and vegetables. The data in Fig. 1

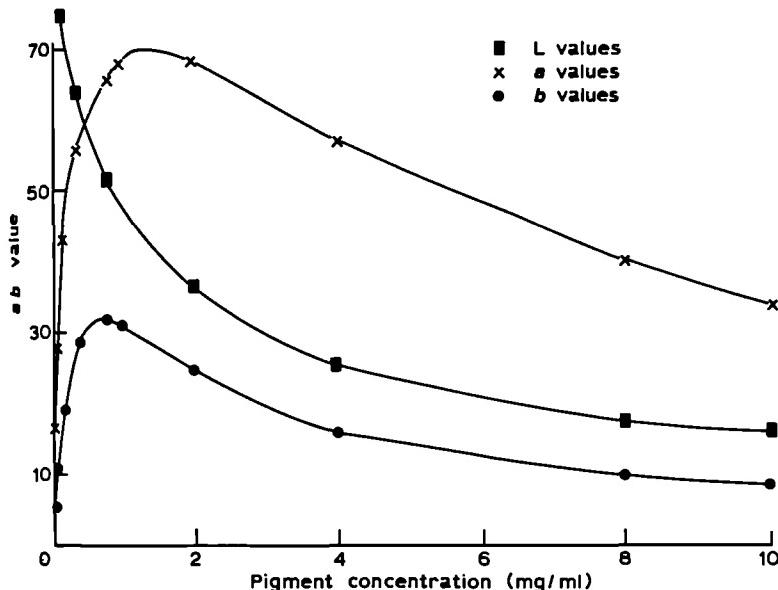


Fig. 7. Plots of Hunter *Lab* versus pigment concentration.

were obtained with a Hunter Colour Difference meter by transmission through an aqueous solution of the pigment. The plots for *a* and *b* show maxima at pigment concentrations of 0.5–2.0 mg/ml. In these 'areas of confusion', it is difficult to know on which part of the curve a particular *a* or *b* value lies. Eagerman *et al.* (1973a) listed eleven different colour solids which all showed areas of confusion. Hunter (1975) introduced the *Lab* scales to expand the scale for low *L* values and reduce the areas of confusion. Eagerman *et al.* (1973b) developed the La_2b_2 scales to eliminate the areas of confusion for dark-coloured beverages (Fig. 8). It is possible to improve the prediction of pigment concentration by a tristimulus reading by making the *a* or *b* reading linear (Eagerman *et al.*, 1973b). Figure 9 shows the '*a*' scale optimized for Cn-3-G and FD+C Red No. 2. The computer optimisation does distort the normal scale as shown in Table 1.

This arrangement makes it possible to read tristimulus values in the normal manner and also calculate pigment concentration from the same data. This procedure is valid for relatively simple colorant mixtures. With more complicated situations such as the prediction of vitamin A content from the beta-carotene content of fruit juices it would be necessary to set up a regression equation relating the colorant value of each of six or more

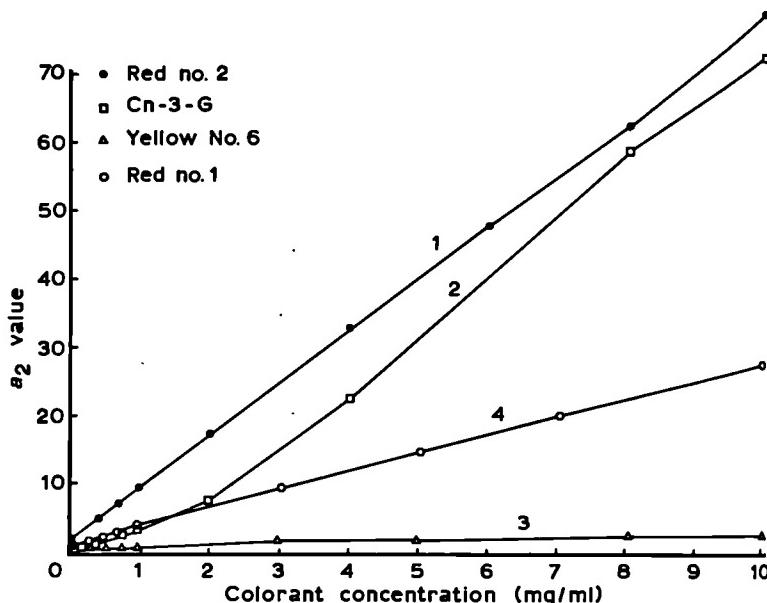


Fig. 8. Plots of a_2 optimised for FD&C Red No. 2.

TABLE I
FORMULAE AND DEGREE OF LINEARITY FOR COLOUR QUALITY MEASURES WHICH ARE LINEARLY RELATED TO COLORANT CONCENTRATION

<i>Colorant</i>	<i>Colour measure</i>	<i>Formula</i>	<i>Coefficient determination</i>
	Hunter <i>a</i>	$\frac{175(1.02X - Y)}{Y^{1/2}}$	
FD&C Red No. 2	<i>a*</i>	$\frac{100X}{Y^{2.30} - 0.5}$	0.9999
Cyanidin-3-glucoside	<i>a*</i>	$\frac{100X}{Y^{1.60} - 1.5}$	0.9996
FD&C Yellow No. 6	<i>a*</i>	$\frac{170(1.02X - Y)}{Y^{3.10}}$	0.9992
	Hunter <i>b</i>	$\frac{70(Y - 0.847Z)}{Y^{1/2}}$	
FD&C Green No. 3	<i>b*</i>	$\frac{120(Y - 0.847Z)}{Y^{1.63}}$	0.9996
FD&C Blue No. 1	<i>b*</i>	$\frac{120(Y - 0.84Z)}{Y^{1.90}}$	0.9994

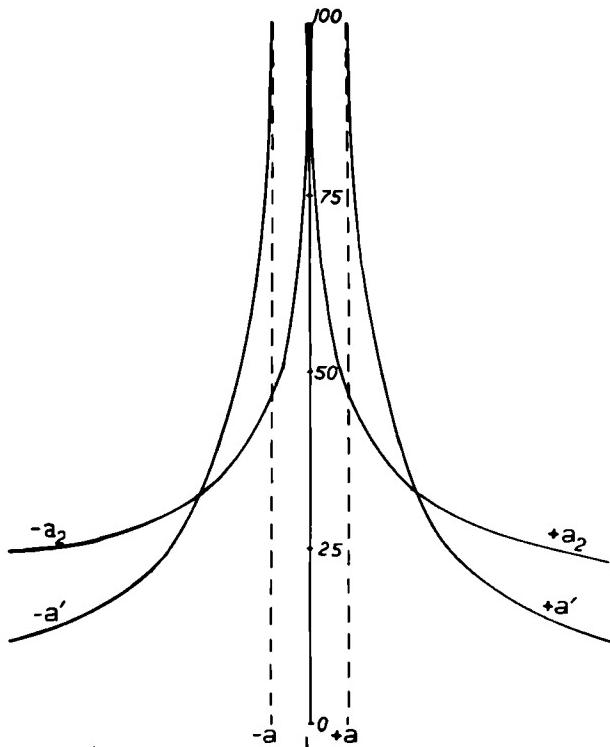


Fig. 9. Diagram showing the expansion of the $a'b'$ and a_2b_2 scales assuming that the normal ab scale has a value of unity.

carotenoid pigments to the overall colour and the contribution of each to the colour. Then the contribution of beta-carotene (the vitamin A precursor) could be determined. It is likely that situations such as this could best be handled by conventional chemical analysis.

SPECIALISED COLORIMETRIC APPLICATIONS

A number of specialised colorimeters have been developed primarily for two reasons. With many food and agricultural commodities visual grading developed from a historical context. With the growth of electronics and instrumental quality measurement, demand arose for instruments which

would duplicate the response of the grader desirably with a one-dimensional scale. The second reason was the hope that the price of an abridged instrument would be less than that of a full-range instrument. Specialised electronic colorimeters have been developed for tomatoes, tomato juice, citrus juice, apples, sugar, wine and cranberries, as well as a large variety of visual instruments for many products. It is beyond the scope of this chapter to discuss these specialised approaches but the trend seems to be to utilise a full-scale instrument equipped with a microcomputer and the ability to read out any desired calculation.

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DISCUSSION

G. V. Merken asked how, if the calibration were changed to accommodate, say, darker products, the results could be communicated to others. F. J. Francis agreed that others must then be informed what had been done, but that the increase in accuracy and sensitivity was worth the complication. In fact, some older instruments used to have a facility for 0-10 expansion of the scale for use with darker products. Modern instruments now have an automatic boost in sensitivity for darker materials but do not always declare that it has been done! M. Kent asked about the independence of the three variables for statistical analysis. Surely X, Y and Z were independent because they were derived from the three *visually independent colours*?

Francis agreed but felt they were not the ones commonly used. *Kent* appreciated the assurance as that was what had been assumed in the Project! *Francis* went on to say that the reason most people used *Lab* was because data reduction was so much easier. However, most systems were mutually interconvertible. Instruments could be designed to provide readout in all the principal scales to choice.

H. Schubert felt that the colour *distribution* of, say, apples was more important than the single colour of a product. How can this best be measured? What is the smallest area of colour which can be measured? Thirty years ago, *Francis* had integrated the colour of part-red, part-green Mackintosh apples by rotating single fruit before a Hunter colorimeter which integrated the skin colour. At the time there were no large-area colour measuring instruments available. Now, instruments are available which can measure the average colour of the top layer of a crate of apples if required—and Mackintosh apples are now red all over! He had encountered the problem of small area colour measurement in connection with the degree of roast of breakfast cereals, 3 mm diameter. An IDL Colour Eye optical system was successfully adapted to measure an area as small as $\frac{1}{8}$ in. diameter.

Collaborative Experiments in Colour Measurement

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SUMMARY

Although many comparative exercises have been performed in the past it was felt necessary that this subgroup should investigate the measure of agreement between the laboratories involved. Using colour standards the variance between laboratories, samples and replicates were studied. Various instrument characteristics were changed to determine their importance. The results are presented in both CIE tristimulus coordinates X, Y, Z and CIELAB colour coordinates.

INTRODUCTION

The interests of the subgroup 'Electrical and Optical Properties of Foods' were from the start of the COST 90bis project predominantly in the area of colour measurement. Participants in this aspect of the subgroup are listed in Table 1 and to them the chairman of the subgroup (MK) expresses his gratitude for their contributions to the collaborative exercise which is described in the following pages.

Although many collaborative tests have been conducted in the past both in the food industry and elsewhere (see Bilmeyer, 1981) it was still felt necessary for this group to determine from the outset the degree of concord between food laboratories when measuring ostensibly identical samples. After a few test runs with arbitrary colour cards a set of 9 colours was chosen from the Swedish National Colour Standard Atlas (Anon, 1982a, b) ('NCS') and purchased for the project by the Swedish Food Institute (SIK).

TABLE 1
INDIVIDUAL AND INSTITUTIONAL PARTICIPANTS IN THE STANDARD COLOUR TRIALS

<i>Participant</i>	<i>Laboratory</i>
V. Merken	Central Laboratory of the Ministry of Economic Affairs, Brussels, Belgium
I. L. Andersen	Danish Meat Research Institute, Roskilde, Denmark
Th. Grünwald	Federal Research Institute for Nutrition, Karlsruhe, Germany
W. Bergthaller	Federal Research Institute for Cereals and Potato Processing, Detmold, Germany
R. Gormley	Kinsealy Research Station, Dublin, Ireland
L. Tijskens	Sprenger Institute, Wageningen, The Netherlands
D. Henshall	Campden Food Preservation Research Association, Chipping Campden, UK
T. Grey	Food Research Institute, Norwich, UK
D. Macdougall	Food Research Institute, Bristol, UK
M. Kent	Torry Research Station, Aberdeen, UK
K. Young	Torry Research Station, Aberdeen, UK
G. E. Hobson	Glasshouse Crops Research Institute, Littlehampton, UK
I. Mcfarlane	Beaconsfield Instrument Co Ltd, Beaconsfield, UK
S. Freeman	Nestle Co Ltd, Croydon, UK
C. Brimelow	Londreco Ltd, Hayes, UK
F. Cooper	H. J. Heinz Ltd, Hayes, UK
I. Brown	Macbeth Instruments Ltd, Sale, UK

TABLE 2
STANDARD COLOURS USED IN THE COST 90bis COLOUR EXPERIMENTS

<i>NCS number</i>	<i>Colour</i>	<i>CIE (nominal)</i>		
		<i>X</i>	<i>Y</i>	<i>Z</i>
5500	Grey	22.26	22.70	26.83
2070B	Blue	14.32	15.85	52.51
4040B	Blue	14.20	15.53	34.02
3070G	Green	5.54	11.59	9.15
4040G	Green	12.54	17.79	17.19
1080Y	Yellow	52.53	55.11	6.89
3040Y	Yellow	34.26	35.53	15.10
1090R	Red	20.81	10.20	3.00
4040R	Red	19.25	14.57	12.09

The colours chosen are detailed in Table 2. These standards were in the form of paper samples 150 mm × 105 mm and were easily distributed to all the laboratories taking part in this part of the exercise (Table 1).

EXPERIMENT DESIGN

Because the equipment in use in the various laboratories was not all of the same type or manufacture the problem of standardisation of the experimental procedures was difficult to resolve. In the event the following procedure was adopted.

1. Illuminant C to be used (CIE, 1931).
2. Measurements to be referred to the 1931 2° standard observer (CIE, 1931).
3. Specular reflection to be excluded.
4. Aperture diameter to be 50 mm or as near this as possible.
5. Coloured papers to be viewed backed by a white tile.
6. Results to be expressed in CIE XYZ tristimulus coordinates.
7. Three replicate measurements of each colour to be made.

In addition certain laboratories investigated the effects of the following variations to this experimental procedure.

1. Specular reflection included or excluded.
2. Paper backed by black, white or grey tile.
3. Aperture size varied.
4. Illuminated area varied.
5. Presence of glass plate between aperture and paper.

The colorimeters used are shown in Table 3 from which it can be seen that predominantly Hunterlab instruments were used. Also in this table the variations in procedure described above are summarised. For the sake of anonymity the order of laboratories is not that in Table 1.

STATISTICAL ANALYSIS OF THE DATA

The data were analysed in the following manner. Mean values of each set of triplicates for every colour, laboratory and instrument setting were calculated (Table 4). The corresponding standard deviations pooled over

TABLE 3
INSTRUMENTAL DIFFERENCES IN THE COLLABORATIVE MEASUREMENTS ON NCS COLOUR STANDARDS

<i>Laboratory</i>	<i>Equipment</i>	<i>Aperture</i> (mm)	<i>Sample</i> <i>backing</i>	<i>Specular</i> <i>reflection</i>	<i>Other</i>
1.1	Hunter D25A	51	black	excluded	
2.1	Gardner XL20	63.5	white	excluded	
3.1	Labscan	44	white	excluded	
4.1	Hunter D25-D2P	28	white	excluded	
4.2	Hunter D25-D2P		white	included	
5.1	Hunter D25-9	50	white	excluded	diffuse spot
5.2	Hunter D25-9	20	white	excluded	diffuse spot
5.3	Hunter D25-9	20	white	excluded	10 mm spot
6.1	Hunter D25-3	45	white	excluded	
6.2	Hunter D25-3	45	white	excluded	2.5 mm glass
7.1	Momcolor	45	white	excluded	
7.2	Momcolor	45	grey	excluded	
8.1	Hunter D25-L	51	white	excluded	
8.2	Hunter D25-L	51	black	excluded	
8.3	Minolta Chromameter	8	white	partially included	
9.1	Hunter D25-A9	51	black	excluded	
10.1	Labscan	51	white	excluded	
13.1	Hunter D25-A9	51	white	excluded	
14.1	Labscan	44	white	excluded	
14.2	Hunter D25-M	51	white	excluded	
14.3	Hunter D25-A	51	white	excluded	
15.1	Gardner XL20	50	white	excluded	
16.1	Hunter D25-M3				
17.1	Macbeth M2020		white	included	
17.2	Macbeth M2020		black	included	
17.3	Macbeth M2020		black	excluded	

colours are in Table 5. Analysis of variance for each variable in each colour was used to estimate separately the variation between replicates and between laboratories. In this scheme the between-laboratories mean square includes a contribution from the between-replicates variance (see Table 6).

Since some differences had occurred in the implementation of the procedures it was necessary to investigate how important such variation might be before drawing conclusions from a comparison of the complete data set. These differences are as described above and are outlined in Table 3.

TABLE 4
MEAN TRISTIMULUS VALUES FOR NINE COLOURS: ALL LABS

Laboratory	Colour								
	5500 (grey)			2070-B (blue)			4040-B (blue)		
	X	Y	Z	X	Y	Z	X	Y	Z
1.1	19.60	19.98	22.78	12.00	13.48	44.60	13.95	15.41	32.49
2.1	19.47	20.17	23.10	10.80	12.93	43.57	13.27	15.27	32.30
3.1	19.58	19.97	22.79	10.95	13.04	43.38	13.65	15.26	32.66
4.1	20.70	21.20	24.50	12.97	14.63	45.57	14.70	16.20	33.40
4.2	20.22	20.62	23.80	13.08	14.52	44.30	14.42	15.72	32.23
5.1	19.26	19.65	22.60	9.99	12.22	43.38	12.87	14.64	32.22
5.2	19.33	19.69	22.57	10.03	12.37	43.79	12.88	14.69	32.22
5.3	19.38	19.72	22.64	10.03	12.11	43.50	13.00	14.68	32.27
6.1	19.16	19.52	22.46	10.06	12.16	44.10	12.88	14.58	32.29
6.2	17.64	17.96	20.60	9.33	11.26	41.65	11.74	13.29	29.85
7.1	20.52	20.82	24.00	12.02	12.97	45.37	14.09	15.40	33.53
7.2	20.51	20.84	24.01	12.05	12.99	45.20	14.10	15.42	33.53
8.1	19.22	19.68	22.61	10.34	12.32	43.49	13.17	14.83	32.49
8.2	19.24	19.70	22.64	10.34	12.28	43.42	13.15	14.81	32.48
8.3	19.85	20.32	23.43	12.66	13.22	44.10	13.82	15.03	31.43
9.1	19.17	19.54	22.51	10.50	12.40	44.61	13.23	14.79	32.67
10.1	19.52	19.90	22.73	10.93	12.86	43.58	13.51	15.07	32.46
13.1	19.13	19.52	22.40	10.48	12.41	44.62	13.03	14.75	32.28
14.1	19.07	19.43	22.29	10.82	12.89	43.21	13.30	14.86	32.07
14.2	19.10	19.50	22.50	10.70	12.70	44.33	13.17	14.87	32.37
14.3	19.03	19.40	22.30	10.10	12.10	43.03	12.93	14.53	32.13
15.1	19.63	20.07	22.87	10.64	12.88	44.45	12.93	14.98	32.12
16.1	19.50	19.85	22.90	10.55	12.58	44.12	13.18	14.78	32.42
17.1	21.98	22.41	25.82	14.21	16.14	46.75	15.65	17.20	34.57
17.2	21.97	22.40	25.81	14.16	16.08	46.52	15.65	17.19	34.56
Mean	19.67	20.07	23.07	11.19	13.02	44.19	13.53	15.13	32.53

(continued)

TABLE 4—*continued*

<i>Laboratory</i>	<i>Colour</i>								
	<i>4040-G (green)</i>			<i>3070-G (green)</i>			<i>3040-Y (yellow)</i>		
	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>X</i>	<i>Y</i>	<i>Z</i>
1.1	11.66	16.88	14.75	4.09	10.19	5.46	31.74	32.80	12.79
2.1	11.50	16.67	14.93	4.37	10.30	5.93	32.13	33.03	13.23
3.1	11.34	16.44	14.57	3.90	9.94	5.54	31.77	32.77	12.27
4.1	12.40	17.60	16.27	5.80	11.67	8.13	32.30	33.70	14.60
4.2	12.21	17.02	15.80	6.21	11.71	8.57	31.44	32.64	14.40
5.1	10.94	16.09	13.95	3.59	9.65	4.66	31.62	32.35	11.72
5.2	10.94	16.14	13.83	3.55	9.69	4.51	31.76	32.20	11.44
5.3	11.01	16.11	13.97	3.61	9.57	4.70	31.72	32.48	11.74
6.1	11.10	16.06	14.10	3.71	9.34	4.78	31.85	32.57	12.00
6.2	10.14	14.77	12.82	3.35	8.54	4.29	29.99	30.58	10.90
7.1	11.90	17.04	15.21	4.49	10.26	5.78	32.71	34.03	13.35
7.2	11.92	17.06	15.22	4.56	10.28	5.84	32.74	34.07	13.40
8.1	11.05	16.19	14.08	3.76	9.83	4.81	31.52	32.60	12.02
8.2	11.02	16.16	14.06	3.73	9.75	4.79	31.56	32.66	12.08
8.3	12.12	16.56	15.98	6.33	11.49	9.24	31.07	32.72	14.08
9.1	11.24	16.30	14.37	3.62	9.45	4.76	31.78	32.74	12.10
10.1	11.18	16.29	14.49	3.82	9.82	5.57	31.65	32.75	12.24
13.1	11.05	16.16	13.86	3.59	9.39	4.53	31.61	32.46	11.80
14.1	11.11	16.10	14.32	3.68	9.36	5.29	31.01	31.95	11.95
14.2	11.13	16.23	14.27	3.70	9.53	4.90	31.30	32.20	12.00
14.3	11.03	16.03	13.77	3.60	9.30	4.33	31.50	32.40	11.60
15.1	11.32	16.56	14.55	3.94	9.80	5.34	32.46	32.95	12.57
16.1	11.21	16.17	14.31	3.87	9.54	5.08	32.04	32.88	12.40
17.1	13.47	18.41	17.45	7.30	13.13	10.17	33.85	35.00	15.92
17.2	13.47	18.41	17.45	7.29	13.07	10.16	33.85	35.00	15.93
Mean	11.50	16.54	14.73	4.38	10.18	5.89	31.88	32.86	12.74

TABLE 4—*continued*

Laboratory	Colour								
	1080-Y (yellow)			4040-R (red)			1090-R (red)		
	X	Y	Z	X	Y	Z	X	Y	Z
1.1	50.13	51.74	5.57	16.95	12.48	10.08	17.41	8.73	2.33
2.1	50.97	52.17	6.07	17.37	13.03	10.67	19.33	10.07	3.67
3.1	50.90	52.29	5.00	17.08	12.52	10.01	18.33	9.03	2.19
4.1	50.37	52.80	7.53	18.20	13.80	11.80	20.13	11.00	5.00
4.2	48.72	50.99	7.70	17.82	13.45	11.60	19.69	10.88	5.20
5.1	51.04	51.96	4.15	16.89	12.28	9.78	18.45	9.15	2.20
5.2	51.21	51.97	3.90	16.97	12.25	9.70	18.24	8.35	1.77
5.3	51.04	52.04	4.11	16.99	12.35	9.83	18.13	9.02	2.16
6.1	50.97	52.06	4.51	16.95	12.41	9.97	18.34	9.15	2.63
6.2	49.49	50.27	4.00	15.65	11.38	9.04	17.39	8.54	2.30
7.1	52.25	54.47	6.45	18.39	13.56	11.67	20.95	10.21	4.76
7.2	52.08	54.49	6.50	18.36	13.55	11.66	20.78	10.20	4.78
8.1	50.41	51.99	4.60	16.95	12.46	10.05	18.72	9.40	2.58
8.2	49.97	51.65	4.47	16.96	12.47	10.05	18.33	9.25	2.56
8.3	49.09	52.03	7.14	17.56	13.89	11.43	20.14	12.12	5.20
9.1	50.63	52.13	4.51	16.97	12.45	10.07	18.28	9.13	2.63
10.1	50.39	52.27	4.59	16.99	12.41	9.79	18.54	9.07	2.04
13.1	50.66	51.82	4.28	16.79	12.27	9.94	17.75	8.79	2.45
14.1	49.95	51.25	4.78	16.63	12.13	9.72	17.82	8.74	2.08
14.2	50.50	51.83	4.77	16.77	12.23	10.00	18.23	9.03	2.53
14.3	51.23	52.43	4.40	16.80	12.30	9.90	18.60	9.23	2.50
15.1	52.29	52.47	5.34	17.48	12.53	10.02	19.70	9.22	2.69
16.1	51.69	52.86	5.17	17.39	12.83	10.34	19.63	10.02	3.09
17.1	52.01	53.92	8.65	19.47	15.07	12.80	22.30	12.78	6.03
17.2	51.76	53.74	8.66	19.47	15.07	12.80	21.80	12.57	6.03
Mean	50.79	52.31	5.47	17.35	12.85	10.51	19.08	9.75	3.26

TABLE 5
REPLICATION STANDARD DEVIATIONS (POOLED OVER NINE
COLOURS)

<i>Lab/data set</i>	<i>s.d. between replicates</i>		
	ΔX	ΔY	ΔZ
1.1	0.047	0.047	0.055
2.1	0.090	0.098	0.069
3.1	0.017	0.018	0.011
4.1	0.067	0.054	0.061
4.2	0.047	0.033	0.064
5.1	0.033	0.029	0.040
5.2	0.065	0.336	0.155
5.3	0.051	0.053	0.050
6.1	0.075	0.068	0.099
6.2	0.057	0.059	0.071
7.1	0.060	0.042	0.051
7.2	0.020	0.023	0.025
8.1	0.028	0.026	0.020
8.2	0.017	0.018	0.024
8.3	0.095	0.090	0.077
9.1	0.091	0.079	0.051
10.1	0.011	0.012	0.013
13.1	0.016	0.019	0.016
14.1	0.032	0.033	0.039
14.2	0.051	0.047	0.043
14.3	0.069	0.038	0.038
15.1	0.043	0.037	0.032
16.1	0.037	0.032	0.042
17.1	0.038	0.033	0.017
17.2	0.037	0.042	0.043

TABLE 6
SOURCES OF VARIATION AND THEIR CONTRIBUTIONS TO THE OVERALL
VARIANCE

<i>Source</i>	<i>Degrees of freedom</i>	<i>Mean square</i>
Laboratories	$n - 1$	MSL
Replicates	$2n$	MSR
MSL is an estimate of	$3\sigma_R^2 + \sigma_L^2$	
MSR is an estimate of	σ_R^2	

n = number of laboratories, σ_R^2 = variance between replicates and σ_L^2 = variance between laboratories.

The data sets dealt with in this manner were as follows:

1. 17.3/17.2 Specular reflection excluded/included.
 2. 5.1/5.2 50 mm aperture, diffuse illumination/20 mm aperture, diffuse illumination.
 3. 5.2/5.3 20 mm aperture, diffuse illumination/20 mm aperture, 10 mm spot.
 4. 6.1/6.2 Direct observation/observation through 2.5 mm glass plate.
 5. 7.1/7.2 White backing/grey backing.
 6. 8.1/8.2 White backing/black backing.
- 17.1/17.2

For each comparison, the differences between values under the two conditions were plotted against their mean for each coordinate and linear regression performed. Where outliers occurred they were removed from the regression. Out of the nine points representing each colour there were sometimes one or even two outliers associated with one or other of the saturated colours. The resulting six regressions are shown in Fig. 1 (a, b, c) in which only the regression lines are shown without the individual points.

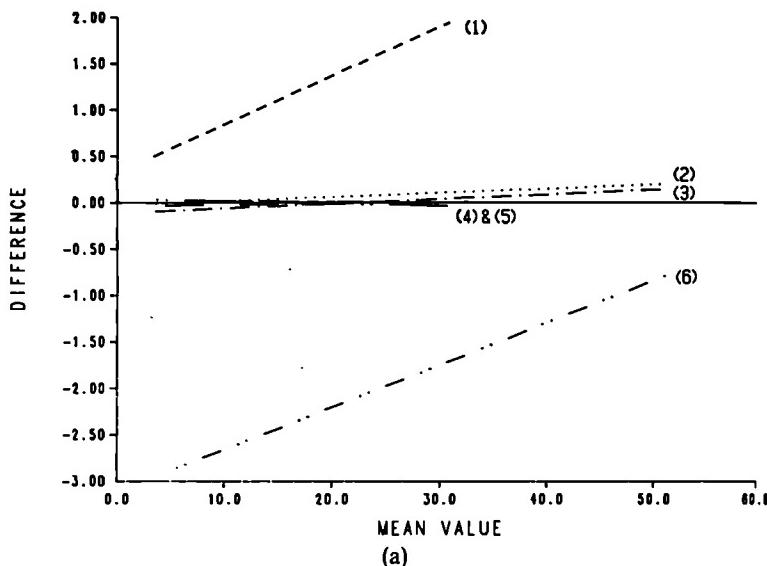
The comparison between specular reflection-included and -excluded led to the expected observation that exclusion generally reduces X , Y and Z values, the effect decreasing as the values themselves increase, i.e. the greatest difference being with the lowest tristimulus values. It should be noted, however, that Bilmeyer and Alessi (1979, 1981) found considerably greater variation between laboratories when the specular component was excluded. This indicates that instruments vary in their abilities to exclude this component.

The comparisons from lab 5 on the effects of aperture size and illumination area show (Figs. 1a, b, c, line 3) small differences of up to 0.35 units in the extremes, depending on the coordinate. These coordinates are generally greater for 20 mm aperture with diffuse illumination than for the 50 mm aperture with diffuse illumination or for the 20 mm aperture with a 10 mm spot size.

As might be expected, the results from lab 6 show that observation through a glass plate reduces the measured values by up to 1.9 units in the case of X , 2.1 for Y and 2.5 for Z , the effect again being greatest for the higher values of the tristimulus coordinates.

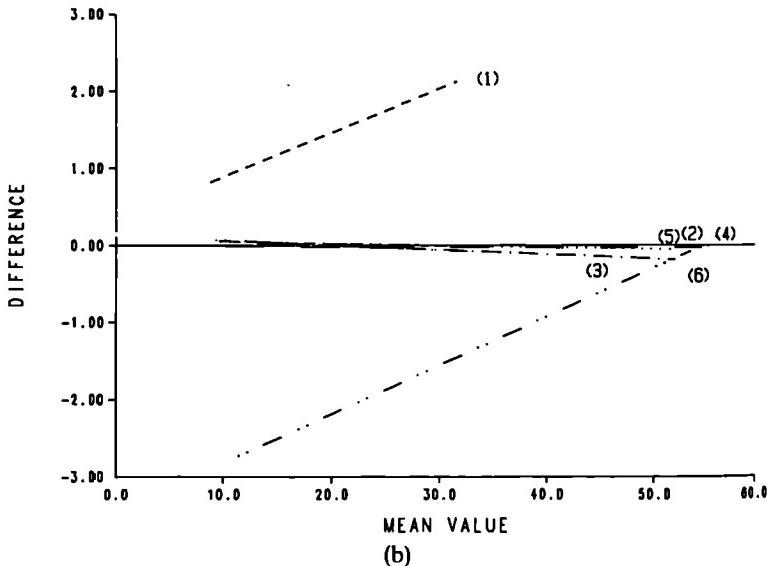
No significant differences occurred between black, white or grey backing tiles. This indicates that the slight apparent translucency of the coloured papers was not important in these measurements.

DIFFERENCES IN X-COORDINATE



(a)

DIFFERENCES IN Y-COORDINATE



(b)

Fig. 1. Regression lines of differences between various experimental procedures versus the mean value, CIE tristimulus coordinates: (a) ΔX versus X ; (b) ΔY versus Y ; (c) ΔZ versus Z . 1, ---, through glass/no glass; 2, ···, diffuse illumination, 50/20 mm apertures; 3, -·-, 20 mm aperture, diffuse illumination/10 mm spot; 4, ——, white/grey backing; 5, ——, white/black backing; 6, -·---, specular reflection excluded/include.

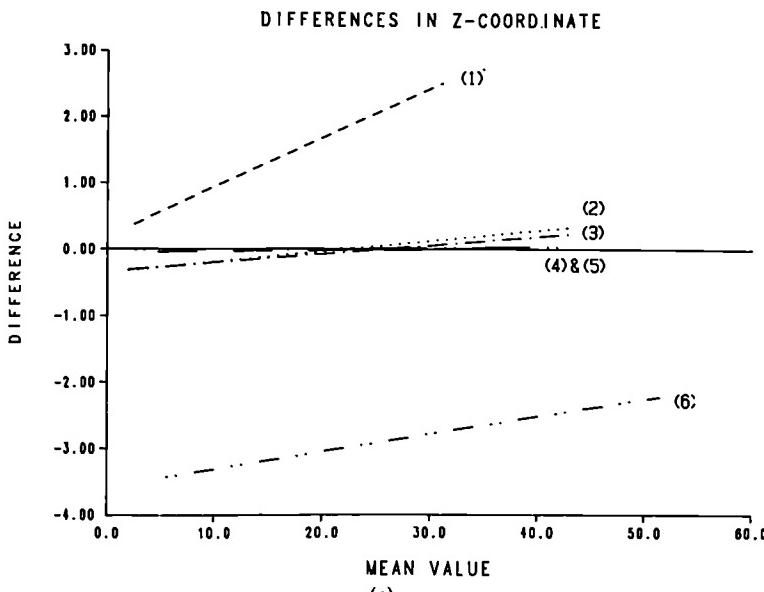


Fig. 1.—contd.

Marcus and Bilmeyer (1974) and Bilmeyer and Alessi (1979, 1981) have shown that tristimulus data are not normally-distributed and so normal statistical analysis may be of limited significance. In the experiments reported here insufficient replicates were measured to test normality adequately but there seems to be no reason to doubt that important observation. It is relevant that conversion of errors through partial derivatives of eqns. (1)-(3) below does not give the same results as converting the tristimulus data to CIELAB followed by the same kind of analysis. For this reason and in order to make the results more meaningful to those using colour measurement in their work it was decided to convert these results from tristimulus coordinates X , Y , Z to coordinates in a uniform colour space, i.e. CIELAB, using the following expressions (CIE, 1978)

$$L^* = 24.991\ 442 \sqrt[3]{Y} - 16 \quad (1)$$

$$a^* = 500(0.216\ 875\ 9 \sqrt[3]{X} - 0.215\ 443\ 5 \sqrt[3]{Y}) \quad (2)$$

$$b^* = 200(0.215\ 443\ 5 \sqrt[3]{Y} - 0.203\ 908\ 9 \sqrt[3]{Z}) \quad (3)$$

These expressions assume 1931 2° standard observer and Illuminant C and are valid only for the condition $X, Y, Z > 1.0$.

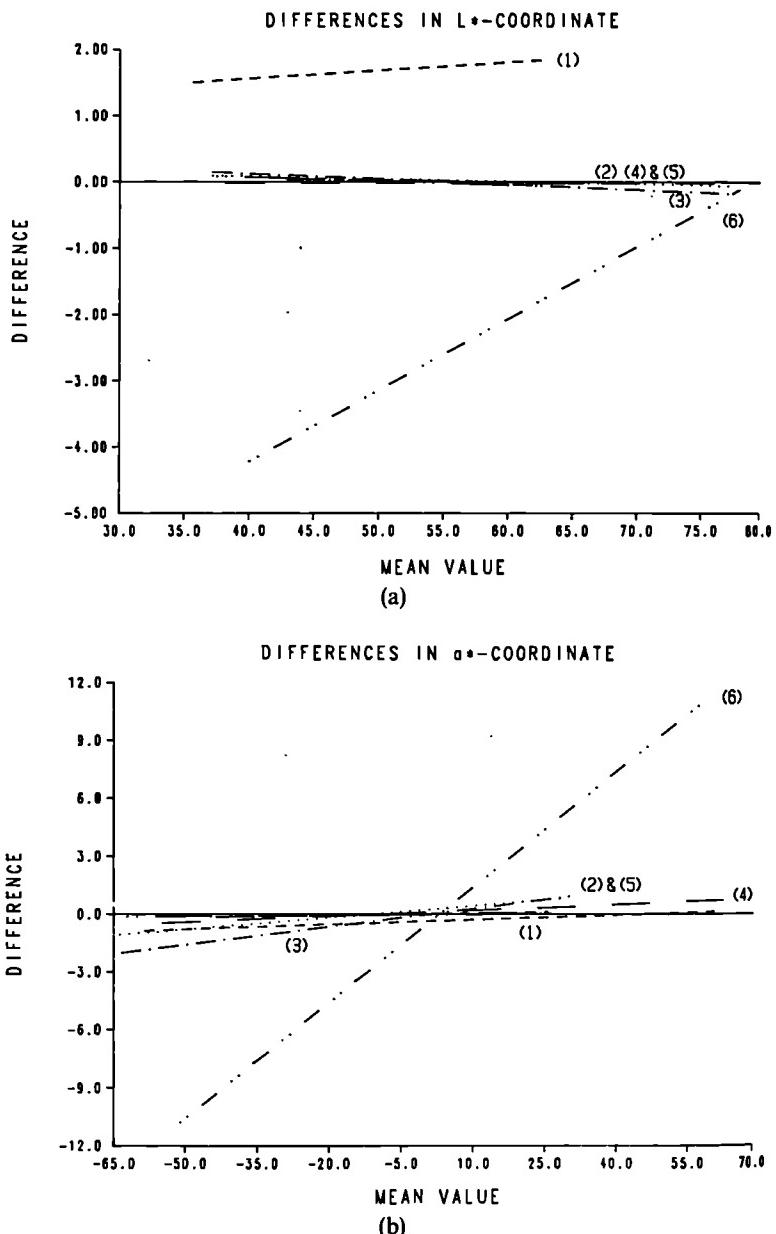
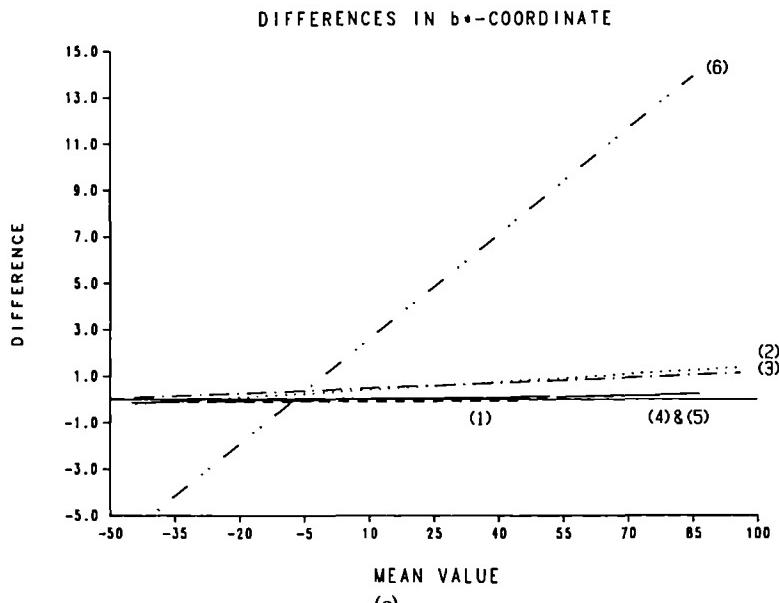


Fig. 2. Regression lines of differences between various experimental procedures versus the mean value, CIELAB colour space: (a) ΔL^* versus L^* ; (b) Δa^* versus a^* , (c) Δb^* versus b^* . 1, —, through glass/no glass; 2, ..., diffuse illumination, 50/20 mm apertures; 3, -·-, 20 mm aperture, diffuse illumination/10 spot; 4, ——, white/grey backing; 5, ——, white/black backing; 6, -·-·-, specular reflection excluded/included.

Fig. 2.—*contd.*

Transformation to CIELAB coordinates exaggerated the effect of inclusion of specular reflection in the results of lab 17. Differences were as much as 11 units in the a^* coordinate and 14 in the b^* .

The differences in the results from lab 6 on the effects of observation through a glass plate were only apparent in a^* . Some of these results are shown in Fig. 2(a, b, c) where differences are plotted against mean values as they were for the tristimulus data.

Given the results of all these collaborative tests it was decided that, to permit examination of variation within a standard method, certain data sets would need to be excluded from the inter-laboratory comparisons, principally those which included the specular reflection although, as mentioned above, exclusion may increase errors. Slight variation in the recommended aperture size could be ignored as could the lightness of the backing tile.

The final selection for comparison therefore contained some 18 different sets of measurements from 15 different laboratories. The means and standard deviations for these selected datasets are shown in Tables 7-12. Dixon's test was used to identify outliers (significant at the 1% level) and

TABLE 7
MEAN TRISTIMULUS VALUES FOR NINE COLOURS: SELECTED LABS AND SETTINGS

Laboratory	Colour								
	5500 (grey)			2070-B (blue)			4040-B (blue)		
	X	Y	Z	X	Y	Z	X	Y	Z
1.1	19.60	19.98	22.78	12.00	13.48	44.60	13.95	15.41	32.49
2.1	19.47	20.17	23.10	10.80	12.93	43.57	13.27	15.27	32.30
3.1	19.58	19.97	22.79	10.95	13.04	43.38	13.65	15.26	32.66
4.1	20.70-s	21.20-s	24.50	12.97	14.63-s	45.57	14.70	16.20	33.40-s
5.1	19.26	19.65	22.60	9.99	12.22	43.38	12.87	14.64	32.22
6.1	19.16	19.52	22.46	10.06	12.16	44.10	12.88	14.58	32.29
7.1	20.52-s	20.82	24.00	12.02	12.97	45.37	14.09	15.40	33.53-s
8.1	19.22	19.68	22.61	10.34	12.32	43.49	13.17	14.83	32.49
8.3	19.85	20.32	23.43	12.66	13.22	44.10	13.82	15.03	31.43-s
9.1	19.17	19.54	22.51	10.50	12.40	44.61	13.23	14.79	32.67
10.1	19.52	19.90	22.73	10.93	12.86	43.58	13.51	15.07	32.46
13.1	19.13	19.52	22.40	10.48	12.41	44.62	13.03	14.75	32.28
14.1	19.07	19.43	22.29	10.82	12.89	43.21	13.30	14.86	32.07
14.2	19.10	19.50	22.50	10.70	12.70	44.33	13.17	14.87	32.37
14.3	19.03	19.40	22.30	10.10	12.10	43.03	12.93	14.53	32.13
15.1	19.63	20.07	22.87	10.64	12.88	44.45	12.93	14.98	32.12
16.1	19.50	19.85	22.90	10.55	12.58	44.12	13.18	14.78	32.42
17.3	19.72	20.13	23.01	11.01	12.70	43.72	13.56	15.03	32.42
Mean	19.51	19.92	22.88	10.97	12.80	44.07	13.40	15.02	32.43
NCS theory	22.26	22.70	26.83	14.32	15.85	52.51	14.20	15.53	34.02
NCS measured	21.63	21.96	25.31	14.45	15.99	51.74	15.04	16.41	34.68
17.1 measured	21.98	22.41	25.82	14.21	16.14	46.75	15.65	17.20	34.57

'NCS theory' data are the Swedish National Standard nominal values whilst 'NCS measured' are values taken from actual production samples.

TABLE 7—*continued*

Laboratory	Colour								
	4040-G (green)			3070-G (green)			3040-Y (yellow)		
	X	Y	X	X	Y	Z	X	Y	Z
1.1	11.66	16.88	14.75	4.09	10.19	5.46	31.74	32.80	12.79
2.1	11.50	16.67	14.93	4.37	10.30	5.93	32.13	33.03	13.23
3.1	11.34	16.44	14.57	3.90	9.94	5.54	31.77	32.77	12.27
4.1	12.40	17.60	16.27	5.80-o	11.67-s	8.13-o	32.30	33.70	14.60
5.1	10.94	16.09	13.95	3.59	9.65	4.66	31.62	32.35	11.72
6.1	11.10	16.06	14.10	3.71	9.34	4.78	31.85	32.57	12.00
7.1	11.90	17.04	15.21	4.49	10.26	5.78	32.71	34.03-s	13.35
8.1	11.05	16.19	14.08	3.76	9.83	4.81	31.52	32.60	12.02
8.3	12.12	16.56	15.98	6.33-o	11.49-s	9.24-o	31.07	32.72	14.08
9.1	11.24	16.30	14.37	3.62	9.45	4.76	31.78	32.74	12.10
10.1	11.18	16.29	14.49	3.82	9.82	5.57	31.65	32.75	12.24
13.1	11.05	16.16	13.86	3.59	9.39	4.53	31.61	32.46	11.80
14.1	11.11	16.10	14.32	3.68	9.36	5.29	31.01	31.95	11.95
14.2	11.13	16.23	14.27	3.70	9.53	4.90	31.30	32.20	12.00
14.3	11.03	16.03	13.77	3.60	9.30	4.33	31.50	32.40	11.60
15.1	11.32	16.56	14.55	3.94	9.80	5.34	32.46	32.95	12.57
16.1	11.21	16.17	14.31	3.87	9.54	5.08	32.04	32.88	12.40
17.3	11.17	16.17	14.91	3.98	9.77	6.29	31.88	33.10	12.74
Mean	11.36	16.42	14.59	4.10	9.92	5.58	31.77	32.78	12.53
NCS theory	12.54	17.79	17.19	5.34	11.59	9.15	34.26	35.35	15.10
NCS measured	12.99	18.07	17.32	6.32	12.66	9.79	33.95	35.14	15.54
17.1 measured	13.47	18.41	17.45	7.30	13.13	10.17	33.85	35.00	15.92

(continued)

TABLE 7—*continued*

Laboratory	Colour								
	1080-Y (yellow)			4040-R (red)			1090-R (red)		
	X	Y	Z	X	Y	Z	X	Y	Z
1.1	50.13	51.74	5.57	16.95	12.48	10.08	17.41	8.73	2.33
2.1	50.97	52.17	6.07	17.37	13.03	10.67	19.33	10.07	3.67
3.1	50.90	52.29	5.00	17.08	12.52	10.01	18.33	9.03	2.19
4.1	50.37	52.80	7.53	18.20	13.80	11.80	20.13	11.00	5.00
5.1	51.04	51.96	4.15	16.89	12.28	9.78	18.45	9.15	2.20
6.1	50.97	52.06	4.51	16.95	12.41	9.97	18.34	9.15	2.63
7.1	52.25	54.47-0	6.45	18.39	13.56	11.67	20.95	10.21	4.76
8.1	50.41	51.99	4.60	16.95	12.46	10.05	18.72	9.40	2.58
8.3	49.09	52.03	7.14	17.56	13.89	11.43	20.14	12.12-s	5.20
9.1	50.63	52.13	4.51	16.97	12.45	10.07	18.28	9.13	2.63
10.1	50.39	52.27	4.59	16.99	12.41	9.79	18.54	9.07	2.04
13.1	50.66	51.82	4.28	16.79	12.27	9.94	17.75	8.79	2.45
14.1	49.95	51.25	4.78	16.63	12.13	9.72	17.82	8.74	2.08
14.2	50.50	51.83	4.77	16.77	12.23	10.00	18.23	9.03	2.53
14.3	51.23	52.43	4.40	16.80	12.30	9.90	18.60	9.23	2.50
15.1	52.29	52.47	5.34	17.48	12.53	10.02	19.70	9.22	2.69
16.1	51.69	52.86	5.17	17.39	12.83	10.34	19.63	10.02	3.09
17.1	50.76	52.91	5.20	17.62	13.06	10.09	20.32	10.26	2.43
Mean	50.79	52.31	5.23	17.21	12.70	10.30	18.93	9.57	2.94
NCS theory	52.53	55.11	6.89	19.25	14.57	12.09	20.81	10.20	3.00
NCS measured	51.85	53.53	7.52	19.60	14.91	12.31	22.80	12.57	5.23
17.1 measured	52.01	53.92	8.65	19.47	15.07	12.80	22.30	12.78	6.03

TABLE 8
 X, Y, Z REPLICATION STANDARD DEVIATIONS (POOLED OVER
 NINE COLOURS)

<i>Lab/data set</i>	<i>s.d. between replicates</i>		
	ΔX	ΔY	ΔZ
1.1	0.047	0.047	0.055
2.1	0.090	0.098	0.069
3.1	0.017	0.018	0.011
4.1	0.067	0.054	0.061
5.1	0.033	0.029	0.040
6.1	0.075	0.068	0.099
6.2	0.057	0.059	0.071
7.1	0.060	0.042	0.051
8.1	0.028	0.026	0.020
8.3	0.095	0.090	0.077
9.1	0.091	0.079	0.051
10.1	0.011	0.012	0.013
13.1	0.016	0.019	0.016
14.1	0.032	0.033	0.039
14.2	0.051	0.047	0.043
14.3	0.069	0.038	0.038
15.1	0.043	0.037	0.032
16.1	0.037	0.032	0.042
17.3	^a	^a	^a

^a Only single measurements provided.

TABLE 9
 X, Y, Z STANDARD DEVIATIONS FOR THE NINE COLOURS

Colour	<i>s.d. between replicates</i>			<i>s.d. between laboratories</i>		
	ΔX	ΔY	ΔZ	ΔX	ΔY	ΔZ
5500	0.039	0.032	0.039	0.47	0.49	0.59
2070-B	0.031	0.037	0.086	0.87	0.59	0.71
4040-B	0.045	0.043	0.059	0.49	0.39	0.46
4040-G	0.040	0.045	0.050	0.41	0.41	0.68
3070-G	0.038	0.054	0.041	0.76	0.68	1.26
3040-Y	0.040	0.043	0.024	0.44	0.49	0.82
1080-Y	0.123	0.100	0.059	0.77	0.69	0.98
4040-R	0.038	0.036	0.032	0.49	0.55	0.65
1090-R	0.061	0.039	0.030	1.01	0.89	1.01

TABLE 10
CIELAB MEAN VALUES FOR NINE COLOURS, SELECTED LABS AND SETTINGS

Laboratory	Colour								
	5500 (grey)			2070-B (blue)			4040-B (blue)		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
1.1	51.81	0.06	1.31	43.47	-8.11	-42.09	46.20	-7.06	-22.90
2.1	52.02	-1.51-0	1.14	42.66	-13.17	-42.36	46.00	-10.52	-22.99
3.1	51.80	0.02	1.28	42.82	-12.77	-41.88	45.99	-8.04	-23.48
4.1	53.17	-0.40	0.81	45.13-s	-8.73	-40.27	47.24	-6.93	-22.31
5.1	51.44	0.00	0.97	41.57	-14.57	-44.03	45.13	-9.40	-24.37
6.1	51.30	0.12	0.96	41.47	-13.62	-45.00	45.06	-8.99	-24.59
7.1	52.75	0.53	0.90	42.72	-4.67	-44.22	46.18	-6.11	-24.30
8.1	51.47	-0.33	1.01	41.71	-12.55	-43.91	45.40	-8.58	-24.27
8.3	52.20	-0.33	0.88	43.10	-1.98-s	-42.19	45.67	-5.60	-22.37
9.1	51.31	0.11	0.91	41.84	-11.88	-44.91	45.35	-7.97	-24.60
10.1	51.73	0.06	1.24	42.55	-11.70	-42.56	45.73	-7.81	-23.66
13.1	51.29	-0.05	1.07	41.86	-12.07	-44.90	45.30	-9.01	-24.17
14.1	51.18	0.13	1.06	42.60	-12.76	-42.08	45.44	-7.92	-23.64
14.2	51.27	-0.08	0.85	42.31	-12.38	-43.81	45.45	-8.82	-24.02
14.3	51.15	0.08	0.99	41.37	-12.91	-43.99	44.99	-9.34	-24.50
15.1	51.92	-0.22	1.34	42.58	-14.00	-43.47	45.61	-11.03	-23.42
16.1	51.67	0.19	0.86	42.12	-12.66	-43.90	45.34	-8.26	-24.29
17.3	51.97	-0.08	1.23	42.30	-10.08	-43.11	45.67	-7.32	-23.68
Mean	51.75	-0.09	1.04	42.45	-11.15	-43.26	45.65	-8.21	-23.75

TABLE 10—*continued*

Laboratory	Colour								
	4040-G (green)			3070-G (green)			3040-Y (yellow)		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
1.1	48.11	-30.39	10.51	38.17	-60.15	21.59	63.99	-1.49	42.54
2.1	47.84	-30.40-o	9.64	38.38	-57.14	19.92	64.19	-0.89	41.79
3.1	47.55	-30.33	9.96	37.73	-60.88	20.50	63.97	-1.25	43.81
4.1	49.01	-29.21	8.75	40.68-s	-49.49-o	15.71	64.72	-2.61	39.50
5.1	47.09	-31.23	10.62	37.20	-63.22	23.59	63.63	-0.34	44.65
6.1	47.05	-29.86	10.18	36.63	-58.99	22.06	63.81	-0.30	44.24
7.1	48.31	-29.63	9.84	38.30	-55.20	20.42	64.98-s	-2.27	42.89
8.1	47.23	-31.01	10.54	37.54	-62.14	23.44	63.84	-1.59	44.22
8.3	47.70	-25.49-o	7.10	40.40-s	-42.54-o	11.67	63.93	-3.64	39.35
9.1	47.37	-30.26	10.12	36.84	-61.19	22.49	63.95	-1.13	44.22
10.1	47.35	-30.56	9.81	37.52	-61.12	19.99	63.96	-1.65	43.89
13.1	47.18	-30.79	10.98	36.73	-61.25	23.45	63.72	-0.77	44.61
14.1	47.10	-30.04	9.76	36.67	-59.63	19.74	63.30	-1.15	43.49
14.2	47.28	-30.62	10.19	36.99	-60.69	22.10	63.51	-0.97	43.72
14.3	47.02	-30.22	10.91	36.56	-60.34	24.13	63.67	-0.95	45.05
15.1	47.70	-30.09	10.27	37.48	-59.25	20.93	64.12	0.56	43.32
16.1	47.19	-29.69	9.96	37.00	-58.19	21.28	64.06	-0.66	43.64
17.3	47.19	-30.02	8.58	37.40	-58.63	16.86	64.23	-2.03	43.10
Mean	47.51	-30.05	9.87	37.68	-58.34	20.55	63.98	-1.29	43.22

(continued)

TABLE 10—*continued**M. Kent and G. L. Smith*

Laboratory	Colour								
	1080-Y (yellow)			4040-R (red)			1090-R (red)		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
1.1	77.12	-1.56	88.25	41.97	28.68	11.84	35.45	59.29	34.62
2.1	77.38	-0.46	86.62	42.81	27.31-o	11.63	37.96	58.44-s	30.15
3.1	77.46	-0.96	91.41	42.03	29.15	12.15	36.04	61.58	36.77
4.1	77.76	-3.66	81.70	43.94	26.85-o	10.51-o	39.58	55.42-s	26.09
5.1	77.26	0.26	95.23	41.65	29.70	12.19	36.28	61.22	37.12
6.1	77.32	-0.17	93.52	41.85	29.17	11.97	36.28	60.62	33.84
7.1	78.74-o	-2.95	87.44	43.60	29.36	10.24-o	38.21	65.24-o	24.89
8.1	77.28	-1.49	93.01	41.94	28.80	11.90	36.74	60.61	35.00
8.3	77.30	-5.11	82.32	44.07	22.93-o	11.71	41.40-s	47.60-o	28.32
9.1	77.36	-1.26	93.61	41.93	28.95	11.82	36.23	60.49	33.77
10.1	77.44	-2.23	93.33	41.85	29.37	12.50	36.11	62.36	38.15
13.1	77.17	-0.39	94.42	41.65	29.21	11.72	35.58	60.55	33.92
14.1	76.83	-0.78	91.38	41.43	29.26	11.97	35.49	61.34	36.68
14.2	77.18	-0.83	92.02	41.58	29.33	11.42	36.05	61.07	34.15
14.3	77.54	-0.44	94.45	41.69	29.07	11.90	36.43	61.32	35.05
15.1	77.56	2.22	90.04	42.05	31.24-o	12.16	36.40	66.98-s	33.61
16.1	77.79	-0.33	91.19	42.15	28.72	12.02	37.87	60.29	33.51
17.3	77.80	-2.92	91.14	42.84	28.49	13.36-o	38.28	61.89	38.95
Mean	77.46	-1.28	90.62	42.30	28.64	11.83	37.02	60.35	33.59

stragglers (significant at the 5% level) in each coordinate of each colour. In Tables 7 and 10 these are indicated by the letters 'o' and 's' respectively.

The between-replicate standard deviations in Tables 8 and 11 were pooled over the nine colours. There are no suspiciously high values and all are of similar magnitude in absolute terms. Expressed as colour differences in CIELAB units they range from 0.05 to 0.33 with a mean of 0.207. It is difficult to make a direct comparison between these tests and those of Bilmeyer and Alessi (1979, 1981) who expressed their results in terms of 'mean colour difference from the mean set of measurements' (MCDM) and in terms of coefficients of variation.

The standard deviations between replicates (pooled over laboratories) and between laboratories (data sets) for each colour are shown in Tables 9 and 12. The three highest between-replicate standard deviations correspond to those coordinates and colours with the highest mean values (saturated red and near-saturated yellow and green) but otherwise there is

TABLE 11
CIELAB REPLICATION STANDARD DEVIATIONS (POOLED
OVER NINE COLOURS)

<i>Laboratory</i>	<i>s.d. between replicates</i>			
	ΔL^*	Δa^*	Δb^*	ΔE
1.1	0.063	0.114	0.061	0.144
2.1	0.102	0.273	0.178	0.340
3.1	0.017	0.038	0.034	0.054
4.1	0.072	0.255	0.081	0.277
5.1	0.037	0.050	0.047	0.078
6.1	0.093	0.148	0.276	0.327
7.1	0.054	0.210	0.095	0.249
8.1	0.027	0.036	0.048	0.066
8.3	0.095	0.148	0.119	0.212
9.1	0.069	0.086	0.070	0.131
10.1	0.015	0.034	0.051	0.063
13.1	0.030	0.050	0.050	0.077
14.1	0.049	0.037	0.074	0.096
14.2	0.072	0.212	0.149	0.269
14.3	0.054	0.201	0.129	0.245
15.1	0.044	0.020	0.063	0.794
16.1	0.044	0.071	0.064	0.105
17.3	a	a	a	a

^aOnly single measurements provided.

$$(\Delta E)^2 = (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2$$

TABLE 12
CIELAB STANDARD DEVIATIONS FOR THE NINE COLOURS

Colour	s.d. between replicates				s.d. between laboratories				s.d. of diff($\Delta E'$)
	ΔL^*	Δa^*	Δb^*	ΔE	ΔL^*	Δa^*	Δb^*	ΔE	
5500	0.036	0.113	0.036	0.123	0.55	0.41	0.17	0.71	
2070-B	0.056	0.139	0.062	0.162	0.88	3.32	1.28	3.67	4.02
4040-B	0.059	0.065	0.038	0.096	0.53	1.37	0.73	1.64	
3070-G	0.094	0.245	0.114	0.286	1.18	4.99	3.13	1.65	6.22
4040-G	0.059	0.098	0.069	0.133	0.53	1.25	0.93	6.00	
1080-Y	0.060	0.177	0.243	0.307	0.41	1.65	3.95	1.89	4.70
3040-Y	0.036	0.051	1.030	1.032	0.40	0.95	1.59	4.30	
1090-R	0.071	0.169	0.152	0.238	1.58	3.99	3.91	1.99	6.14
4040-R	0.054	0.127	0.061	0.151	0.82	1.69	0.67	5.81	
Mean				0.28				3.07	5.27

$$(\Delta E)^2 = (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2$$

For two similar colours 1 and 2 $(\Delta E')^2 = (\Delta E_1)^2 + (\Delta E_2)^2$.

no clear dependence of variation on mean value so coefficients of variation are not uniform. The mean of the between-laboratories standard deviation is an order of magnitude greater than that between replicates.

It should be remarked that, as can be seen in Table 7, the means of the values measured in these tests differ significantly from the values quoted by the Swedish National Colour Standard (Anon., 1982a,b). As already seen, however, there is a very significant difference when the specular component of the returned light is included in the measurement. This was well demonstrated by sets 17.1 and 17.2 (Table 4) which include this component and are very close to the Swedish figures. This is highlighted in Table 7. When it is realised that the Swedish standards are measured at source under conditions of specular light inclusion then this discrepancy is explained. Laboratory 17, when repeating the measurements without the specular component (17.3), obtained results which agreed closely with the mean values reported here and are included in the data of Tables 7-13.

DIFFERENCE MEASUREMENTS

Many colour measurements are made with reference to a standard colour tile used as a 'hitching post'. It seems fairly obvious that measurements made in this way should gain in accuracy due to the removal of any instrument bias and the smaller calibration range required of the instrument. Just how much can be gained can be demonstrated by these

collaborative experiments. From the set of nine colours excluding the grey there were four pairs of red, green, yellow and blue respectively.

Examination of the variation in the differences between members of each pair is a useful way of showing this improvement.

In considering differences it is only possible to make meaningful comparisons between means and not between individual replicate determinations which are not matched. No one of the three determinations on one card has any connection with any one of three measurements made on a related card. The lowest level therefore at which differences can be examined is at the means of these triplicates. Analysis of variance on all data for each pair of cards allows estimates to be obtained of the standard deviation of the laboratory-colour interaction. This is a measure of how the difference varies between the laboratories and is the object of the exercise.

Mean values for each card, the mean difference, the range of differences from all the labs and the standard deviation just described are all given in Table 13. It will be seen that, as expected, there is an improvement in the standard deviation between laboratories for the difference measurement as compared to the absolute measurement since any bias that is introduced in a given laboratory (and which of course varies from laboratory to laboratory) is removed. The results are similar to those quoted by Bilmeyer (1981) in that, overall, the mean standard deviation is about 10% of the measured difference but they should not be compared directly since the colour differences he quotes are only 2-3 CIELAB units whereas here the differences range from 2 to 50 units.

No correlation is evident in tristimulus coordinates between the magnitude of any variable and that of the standard deviation. In CIELAB it is possible that the variation becomes smaller with increasing L^* , increasing a^* and decreasing b^* but this cannot be confirmed with such a limited quantity of data.

Finally it is worth quoting Bilmeyer (1981) again with reference to sources of variation and degree of absolute accuracy. He lists in decreasing order of importance:

1. uninformed operators (sic);
2. different reference white standards;
3. variation in chromatic reference standards;
4. integrating sphere conditions.

To this might be added, of great importance, optical geometry especially with regard to specular exclusion. It should also not go unheeded that item

TABLE 13
DIFFERENCES BETWEEN CARDS OF SIMILAR COLOUR

Colour	X	Y	Z	L*	a*	b*	ΔE	abs ΔE'
Mean 2070-B	10.97	12.80	44.07	42.77	-11.15	-43.27		
Mean 4040-B	13.40	15.02	32.43	45.65	-8.21	-23.76		
Mean differences	-2.43	-2.22	11.64	-3.12	-2.94	-19.51		
Range of differences	-2.88	-2.51	10.72	-3.69	-5.16	-20.73		
s.d. interactions	-1.16	-1.57	12.67	-2.11	+3.62	-17.96		
	0.32	0.18	0.40	0.29	1.62	0.51	1.72	4.02
Mean 4040-G	11.36	16.42	14.59	47.51	-30.05	9.87		
Mean 3070-G	4.10	9.92	5.58	37.68	-58.34	20.55		
Mean differences	7.26	6.50	9.02	9.84	28.29	70.69		
Range of differences	5.79	5.07	6.75	7.30	17.05	-13.22		
s.d. interactions	7.61	6.85	9.61	10.53	32.00	-4.57		
	0.30	0.30	0.46	0.58	2.74	1.57	3.21	6.22
Mean 3040-Y	31.78	32.78	12.53	63.98	-1.29	43.23		
Mean 1080-Y	50.79	52.31	5.22	77.46	-1.28	90.63		
Mean differences	-19.02	-19.53	7.30	-13.48	-0.00	-47.40		
Range of differences	-19.83	-20.44	6.90	-13.87	-1.66	-50.59		
s.d. interactions	-18.02	-18.94	7.65	-13.04	+1.47	-42.20		
	0.36	0.25	0.16	0.15	0.51	1.71	1.79	4.70
Mean 4040-R	17.21	12.70	10.30	42.30	28.65	11.83		
Mean 1090-R	18.93	9.57	2.94	37.02	60.36	33.59		
Mean differences	-1.72	3.13	7.35	5.28	-31.71	-21.76		
Range of differences	-2.71	1.77	6.23	2.66	-35.88	-25.66		
s.d. interactions	-0.46	3.75	7.82	6.52	-24.67	-14.65		
	0.42	0.30	0.28	0.61	1.72	2.36	2.98	6.14
Mean							2.43	5.27

Abs ΔE' from Table 12. $(\Delta E')^2 = (\text{s.d. } L^*)^2 + (\text{s.d. } a^*)^2 + (\text{s.d. } b^*)^2$.

was considered by Bilmeyer to have contributed up to 0.5 CIELAB units to the error in collaborative measurements.

CONCLUSIONS

Perhaps the most important conclusion which must be drawn is also the most obvious one and has been stated often. If colour data are to be transferable, i.e. if laboratories wish to compare results obtained on similar samples, then the measurement system must be very carefully defined. This is especially true where different kinds of instruments are being used. Given the fairly wide range of instruments used in this study, remarkable agreement between laboratories was achieved but it is felt that this agreement could have been even better had much more rigorous standardisation of method taken place. As might be expected, the use of a reference colour for colour difference measurements would clearly be beneficial in improving accuracy.

Thus where the effect on the measurements of variation of certain instrument characteristics could be studied, it was clear which were, for this type of uniform sample, unimportant variables and which were not. As will be seen in other contributions in this volume when foods themselves are investigated instead of reference standards, then even greater care in this respect is required.

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DISCUSSION

M. Ruegg asked if any differences due to continuous versus flash illumination had been found. *M. Kent*: Although the differences due to different illuminants (e.g. 'C' versus D65) were significant, when, say, illuminant 'C' was specified, he expected the required illumination to be provided whether in continuous mode or flash, and had not observed any departure from this in the results. *F. J. Francis* went further and said this was a common problem with instruments. It did not matter *what* illuminant was used, provided the right combination of illuminant, filters and photocell were used and the instrument was itself calibrated by the manufacturers to give a reading in terms of (say) *X*, *Y*, *Z*. He said that the system which had been used in the Project was an 'ideal' one using colour cards with dense pigments and good reflectance, but foods do not satisfy these conditions and could be expected to show greater variability in results. This difference should be borne in mind.

Collaborative Measurements on the Colour of Light-scattering Foodstuffs

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SUMMARY

Collaborative trials on the measurement of the colour of foods were undertaken with a view to investigating the effects of sample variables on the measured Hunter L, a, b values. Results were collected on samples of tomato paste, evaporated milk, raspberry pulp and orange juice. In these samples the water content was varied by progressive dilution. In addition, particulate foodstuffs (dried potato and paprika) were studied with regard to their particle size ranges.

Comparison was also made between absolute measurement, with reference only to black and white standards, and colour difference measurement, with reference to a defined standard colour card, for tomato paste samples. Improvement in accuracy was found in the latter case.

INTRODUCTION

After completing the work reported in Chapter 22 by Kent and Smith, the participants of the electrical and optical properties subgroup chose to investigate potential sources of error in the measurement of the colour of foodstuffs in which there was a degree of light scattering. It was again required to know how much variation still occurred between laboratories when as much as possible of the technique was standardised. Some of the results obtained arose from investigation of the variation due to instrument characteristics such as aperture size and these are discussed in Chapter 24 by Brimelow in relation to measurement in an industrial context. There

were particular effects due to the dilution and optical density of light-scattering liquids which are discussed in more detail in Chapter 25 by MacDougall.

It has already been shown in Chapter 22 that certain experimental variables can cause variations of a specific kind and that with careful control such variations can be eliminated. Those results were, of course, obtained on virtually flat, opaque samples with only surface reflection. Little or no effect of the lightness of the backing tile was noted in those experiments so light penetration of the paper was not a problem. The scattering of light within materials is, however, of prime importance in measurements on foods, particularly dilute suspensions and powders. Apart from the possibility of wavelength-dependent scattering or absorption changing the spectral content of the detected light, there is also the possibility that some light may escape detection entirely by being scattered beyond the boundaries of the sample (Little, 1964; Hunter, 1978). If only reflected light is to be studied and not some combination of reflection and transmission, as in the Kubelka-Munk type of analysis (see, for example, Francis and Clydesdale, 1975), then it is very important to be aware of the effects of other variables on the system. Thus, for liquid

TABLE 1

<i>Participant</i>	<i>Tomato paste</i>	<i>Evaporated milk</i>	<i>Raspberry pulp</i>	<i>Potato powder</i>	<i>Pepper</i>	<i>Orange juice</i>
R. Gormley, Kinsealy Research Centre, Dublin, Ireland	x					
D. Henshall, Campden Food Preservation Research Association, Chipping Campden, UK	x					
D. MacDougall, Food Research Laboratory (Bristol), UK	x	x	x	x		
Th. Grunewald, Federal Research Institute for Nutrition, Karlsruhe, Germany	x	x		x		
W. Bergthaller, Federal Research Institute, for Cereals and Potato Processing, Detmold, Germany	x	x	x	x		x
M. Kent, Torry Research Station, Aberdeen, UK	x	x	x	x	x	x
G. Hobson, Glasshouse Crops Research Association, Littlehampton, UK	x	x	x			x
C. Brimelow, Londreco Ltd, Hayes, Middlesex, UK	x	x	x	x		x
F. Cooper, H. J. Heinz Ltd, Hayes, Middlesex, UK	x	x				x
I.-L. Andersen, Meat Research Institute, Roskilde, Denmark	x					

suspensions, the effects of dilution on the colour of tomato paste, evaporated milk, raspberry and orange juice were studied. These are all important commodities in the European and World context. For example, in 1985 the total quantity of tomato paste produced in Europe had a value of *ca* 550 000 000 ecu (£390 000 000) (see Chapter 24).

Also studied was the effect of the particle size of powders, and for this dried potato and red peppers were used.

The participants in these experiments and the foodstuffs studied are listed in Table 1.

EXPERIMENTAL DETAILS

Of the eleven instruments used by the different laboratories, eight were Hunter devices (five 'A' head, two 'L' head and one Labscan). Of the remainder, two were Gardner XL-20 and one Momcolor, an instrument of Hungarian manufacture.

For the measurements the following standard conditions were adopted:

- (a) illuminant C;
- (b) 1931 2° Standard Observer;
- (c) 50 mm aperture;
- (d) glass sample cells of 60 mm diameter with 2·5 mm thick base;
- (e) sample covered by a black light-absorbing box to eliminate extraneous light;
- (f) calibration performed through a glass plate 2·5 mm thick of the same material as the sample cell; and
- (g) ambient temperature.

The foodstuffs investigated in this study were as follows:

(a) 200-g cans of tomato paste, heat processed for various lengths of time from 0 to 3 h. All samples were stored after distribution at a temperature of +1°C. When the cans were eventually opened for the experiments, any discoloured material around the edges of the sample was discarded before measurement. Measurements were made at the original concentration of 30% TSS (total soluble solids) and at dilutions down to 8% TSS using deaerated distilled water. Provision of these samples by Londreco Ltd, UK, is appreciated.

The tomato paste measurements were repeated in a colour-difference mode using a red-coloured card as a reference point ('hitching post').

Standard card (5050 Y80R) from the Swedish National Standard colour atlas (Anon., 1982) was chosen for its close resemblance to tomato paste. It was measured by each laboratory, as described in Chapter 22, with a view to its use as a common reference. The tristimulus values then used for calibration were $X = 9.87$, $Y = 6.33$, $Z = 1.9$, which were the mean of the values for the card from all the laboratories. Whether this is an accurate figure or not is irrelevant at this point since the object was to compare the colour difference method with the absolute colour method. This kind of comparison was only performed on the tomato paste.

(b) Evaporated milk ('Ideal') was provided for the project, also by Londreco/Nestlé Ltd. Measurements were made at the concentration shown in Table 2 and at serial dilutions of $0.8^n \times C$, where C is the initial concentration and $n = 0, 1, 2, \dots, 6$ or occasionally greater integers.

The measurement of the evaporated milk samples in relation to a white colour standard might be regarded as being a colour *difference* method and the variation between laboratories should consequently be small.

(c) Orange juice was supplied by the Campden Food Preservation Research Association (CFPRA) and (after receipt) was diluted for

TABLE 2a
COMPOSITION OF LIQUIDS USED

Sample	Protein ($N \times 6.25$) (%)	Carbohydrate (sugars expressed as sucrose)	Water (%)	Fat (%)	Other % (e.g. fibre, pectin, etc.)	Ash (%)
Evaporated milk	8.2	12	68	9.0	2.5	—
Raspberry pulp	1.48	4.04	85.78	—	8.31	0.39
Orange juice	1.64	28.50	58.84	—	9.55	1.47
Tomato paste	5.77	15.58	69.89	—	5.50	3.33

TABLE 2b
PARTIAL COMPOSITION OF POWDERS USED

Sample	Protein	Sugar (expressed as sucrose)	Starch	Water	Ash
Paprika	17.16	—	—	10.61	9.09
Potato					
Powder 1	6.67	1.52	71.72	10.16	3.43
Powder 2	8.66	—	74.48	10.46	3.5

measurement in the same way as the milk samples. It was frozen and distributed via the normal mail services in insulated containers, during which some thawing occurred but samples were thus kept at reasonably low temperatures during distribution.

(d) Raspberry pulp was prepared from raspberries provided by the Scottish Crops Research Institute and was also distributed, and diluted, as in (c) above. A check conducted in the author's Scottish laboratory confirmed that no significant change in colour took place in 2 weeks' storage at room temperature. Some separation of the solid matter and mould growth had little or no effect if the samples were stirred prior to measurement.

(e) Potato powders were supplied by the Federal Research Centre for Cereal and Potato Processing. These were of different origins, the first being described as an intense-yellow, semi-technical product (Berghaller *et al.*, 1983) blanched in boiling water for 165 s and dried at constant air velocity in two steps, initially at 78°C and subsequently at 55°C.

The second, a pale yellow material, was of industrial origin treated with sulphur dioxide. These powders were fractionated by sieving into different particle size ranges from <250 µm to >1000 µm.

(f) Dried pepper (paprika) of three different particle sizes were prepared for the project by P. Fito of the Polytechnical University Valencia. The particle sizes were nominally 143, 180 and 260 µm, respectively, and were obtained by milling and sieving.

The composition of the liquid foodstuffs is shown in Table 2a and of the powdered samples in Table 2b. The analyses were performed by staff of Londreco Ltd.

RESULTS

I. Liquid Suspensions

(a) Tomato paste

The effect of cooking time on the colour of the tomato paste samples is shown in Fig. 1 and the measurements along with standard deviations are presented in Table 3. The effect of concentration on the results is shown in Fig. 2 and tabulated in Table 4.

Figure 2 shows the *a* value to pass through a maximum as concentration is increased and both the *L* and *b* values to fall with increasing concentration. It should be noted that dilution to *ca.* the USDA-recommended

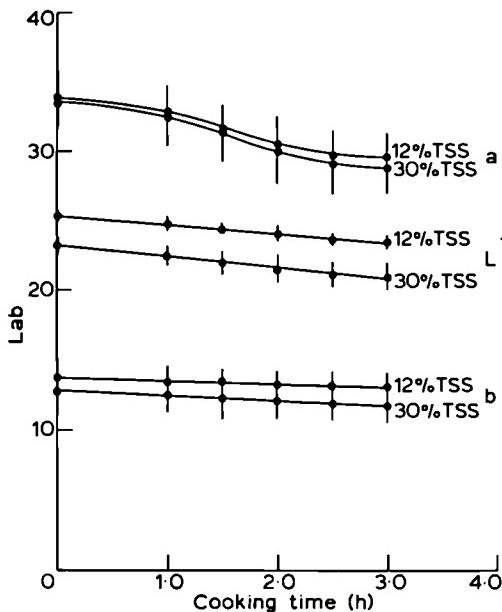


Fig. 1. Effect of cooking time on the colour of tomato paste. Samples measured at TSS as processed (30%) and diluted (12%). Hunter *L, a, b* values versus cooking time in hours.

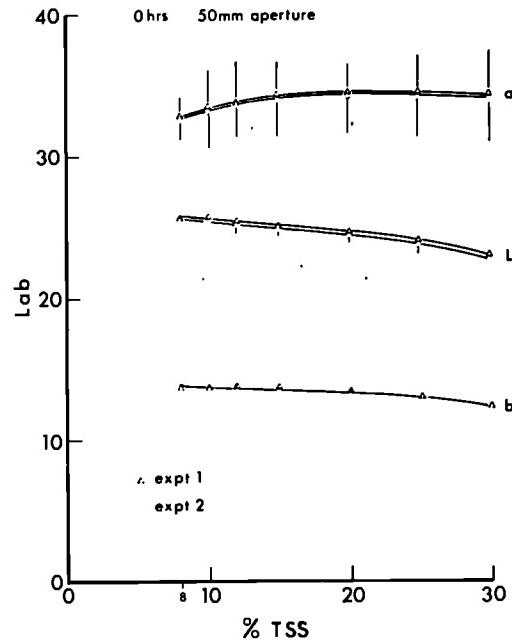


Fig. 2. The effect of dilution on the measured Hunter *L, a, b* values for tomato paste with an aperture of 50 mm. Experiment 1, black and white reference standards. Experiment 2, red reference standard. 8% TSS is marked to indicate (*ca.*) the concentration used in the USDA standard method.

TABLE 3
Hunter L, a, b MEAN VALUES AND STANDARD DEVIATIONS FOR TOMATO PASTE AS A
FUNCTION OF THE COOKING TIME
(absolute measurements, using black and white reference standards)

Cooking time (h)	0	1	1.5	2.0	2.5	3.0
30% TSS						
Number of labs	10	10	9	10	10	10
L	23.07	22.44	21.89	21.55	21.15	20.96
ΔL (s. dev.)	0.85	0.93	1.11	1.04	1.05	1.01
a	33.83	32.39	31.26	29.83	28.94	28.85
Δa (s. dev.)	2.27	2.21	2.14	2.57	2.32	2.00
b	12.66	12.44	12.29	11.97	11.74	11.81
Δb (s. dev.)	1.14	1.25	1.45	1.21	1.31	1.24
12% TSS						
Number of labs	10	10	10	10	10	10
L	25.23	24.73	24.27	24.01	23.70	23.52
ΔL (s. dev.)	0.32	0.45	0.59	0.44	0.23	0.57
a	33.58	32.57	31.52	30.44	29.68	29.51
Δa (s. dev.)	2.11	2.26	2.22	2.21	2.00	1.92
b	13.63	13.53	13.44	13.21	13.03	13.09
Δb (s. dev.)	0.93	0.97	0.39	0.95	1.02	0.97

TABLE 4
Hunter L, a, b VALUES FOR TOMATO PASTE AS A FUNCTION OF CONCENTRATION
(absolute measurements)

% TSS	30	25	20	15	12	10	8
Number of labs	6	6	6	6	7	6	6
L	22.74	23.70	24.23	24.79	25.14	25.34	25.51
ΔL (s. dev.)	0.35	0.43	0.32	0.33	0.29	0.30	0.42
a	33.98	34.01	34.09	34.04	33.71	33.19	32.56
Δa (s. dev.)	3.06	2.71	2.59	2.59	2.50	2.79	1.41
b	12.13	12.78	13.02	13.31	13.51	13.54	14.01
Δb (s. dev.)	1.24	1.22	1.23	1.10	1.09	0.53	1.35
Difference measurement							
Number of labs	7	7	7	7	7	7	7
L	22.86	23.87	24.54	24.99	25.37	25.59	25.76
ΔL (s. dev.)	0.41	0.38	0.49	0.49	0.51	0.58	0.51
a	34.12	34.31	34.29	34.16	33.78	33.40	32.77
Δa (s. dev.)	1.23	1.24	1.14	1.27	1.33	1.41	1.28
b	12.40	12.90	13.23	13.57	13.68	13.75	13.87
Δb (s. dev.)	1.56	1.42	1.39	1.35	1.26	1.23	1.24

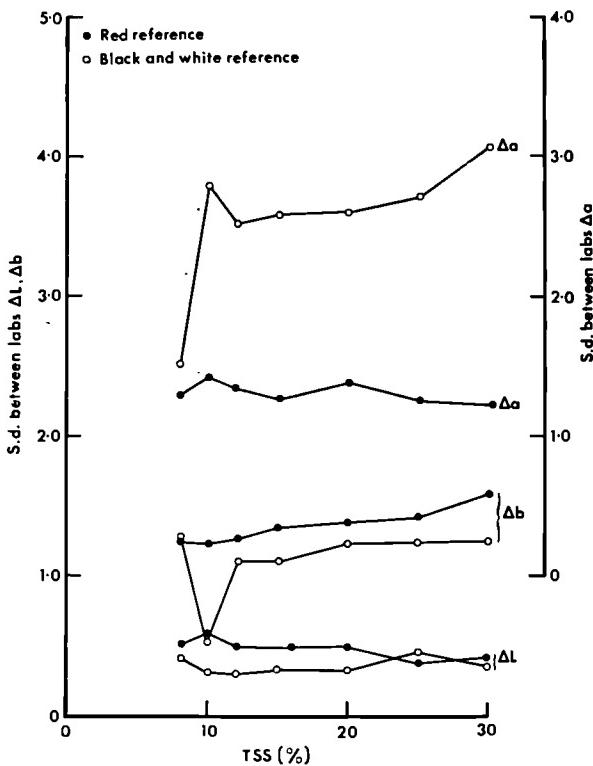


Fig. 3. The between-laboratories standard deviations for the two different colour references versus concentration showing the reduction when a red reference is used as a 'hitching post'.

level (Anon., 1978) of 8% TSS for colour assessment corresponds to a region in which the gradient is steepest (see also Chapter 24).

The two sets of data shown relate to absolute measurement against black and white tiles (expt 1) and to colour difference measurement using the red card as reference (expt 2). The close agreement apparent in the \bar{L} , \bar{a} , \bar{b} (i.e. mean) values from these two experiments is fortuitous since samples of different origin were studied in the two cases. In Fig. 3 the between-laboratory standard deviations for these results have been plotted versus concentration. It can be seen how the spread of results in the determination of a is considerably reduced by the reference method. A similar improvement was also shown in Chapter 22 in respect of measurement of

related pairs of standard colours. The results have a scatter some three times less than that for the 'absolute' measurements. On the other hand, the scatter of the other coordinates L and b is hardly changed. Although the absolute values of these errors is of the same order of magnitude for all three coordinates, when they are expressed as coefficients of variation, that is as a percentage of the mean value, then those for the b value, because of its smaller value, appear larger. Represented in this way, the deviation of b can be as high as 13%. This means that although there is improvement in the accuracy of determination of a , from 8 to 10% deviation down to 3 to 4% deviation, that improvement is to a large extent lost when the ratio of a/b is taken, as is common in the industry.

(b) Milk

The results for the evaporated milk also show a maximum as the concentration increases, in this case in L . These results are plotted in Fig. 4, where the logarithmic scale for concentration spaces the points uniformly in the horizontal direction. Table 5 also contains these results along with the between-laboratories standard deviations.

(c) Raspberry pulp

A problem encountered with the raspberry pulp was the tendency for the solids to settle out, a tendency which proceeded as the dilution increased. Consequently only a small range of dilutions was studied but even in this range similar behaviour to that of the other liquids was seen. These results are plotted in Fig. 5 and tabulated in Table 5.

(d) Orange juice

The results for this sample were the most interesting since both L and b exhibited a pronounced peak in value as the dilution increased. This can be seen in Fig. 6. Such effects are further explored by MacDougall in Chapter 25. Note also how the between-laboratories standard deviation for L and b in Table 5 varies with dilution. For \bar{a} , the measurements agree more closely the more dilute the sample. For \bar{L} and \bar{b} , a minimum scatter occurs at the middle of the range. This observation is not affected by the fact that fewer laboratories contributed results at the very dilute end of the range. It probably results from relative shifts of the curve from each laboratory which would have the greatest effect on the overall means at the steep extremes of the curves. As might be expected, then, disagreement between laboratories can increase if dilution of the sample increases the gradient of the effect of concentration on the colour variable.

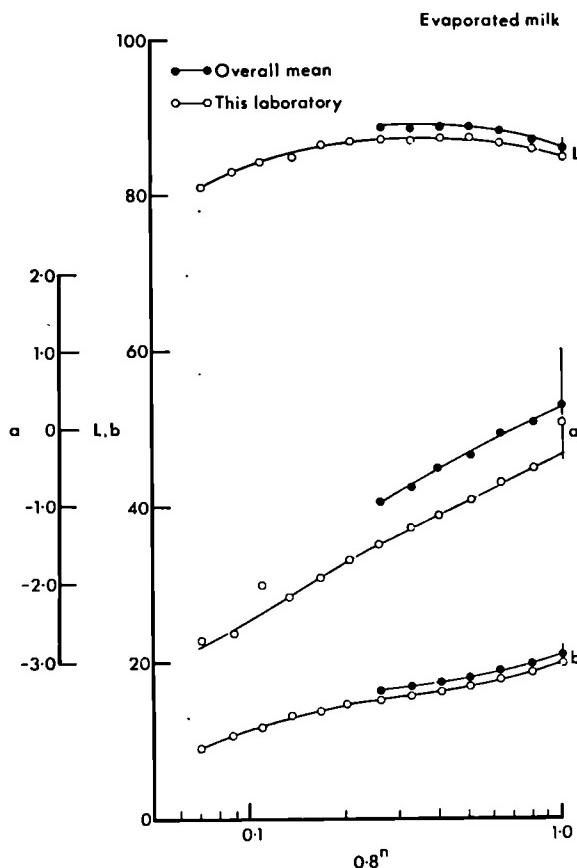


Fig. 4. The effect of dilution on the measured Hunter L , a , b values for evaporated milk at an aperture of 50 mm. The logarithmic relative concentration scale spaces the serial dilutions uniformly. The actual concentrations can be found by multiplying the plotted relative value by the concentration before dilution. The results from one lab (this author's lab) are included to show the extension of the curves to lower concentrations.

2. Particulate Solids

(a) Potato powders

Although the effects of aperture size on the measurement of light-scattering liquids and pastes are discussed in a separate chapter, the effects of aperture size on the measurement of powder colour will be briefly discussed here.

The results for the potato powders are shown in Table 6. Those for

TABLE 5
EFFECT OF DILUTION ON THE COLOUR OF VARIOUS FOODSTUFFS EXPRESSED IN Hunter *L, a, b* COORDINATES
(*n* is the degree of dilution as explained in the text; *N* is the number of laboratories/data sets used)

<i>n</i>	0	1	2	3	4	5	6	7	8	9	10	11	12
Raspberry pulp													
<i>N</i>	6	6	6	6	5	5	2						
<i>L</i>	14.52	15.14	15.65	16.31	17.18	17.74	18.94						
ΔL (s. dev.)	0.37	0.62	0.65	0.95	1.15	0.94	0.52						
<i>a</i>	24.55	24.50	24.14	23.89	23.11	22.63	22.72						
Δa (s. dev.)	0.88	1.06	1.19	1.35	1.23	1.39	1.12						
<i>b</i>	5.54	5.68	5.77	6.03	6.18	5.93	6.65						
Δb (s. dev.)	1.26	1.19	1.20	1.15	1.09	1.23	0.65						
Evaporated milk													
<i>N</i>	7	7	7	7	7	7	5	1	1	1	1	1	1
<i>L</i>	86.41	87.52	88.23	88.66	88.87	88.93	88.76	86.65	86.11	85.21	83.98	92.61	80.69
ΔL (s. dev.)	1.17	1.18	1.22	1.27	1.30	1.39	1.91	0.02	0.01	0.02	0.19	0.01	0.03
<i>a</i>	0.41	0.07	-0.07	-0.39	-0.54	-0.77	-0.92	-1.70	-1.96	-2.21	-2.07	-2.62	-2.75
Δa (s. dev.)	0.87	0.80	0.68	0.69	0.63	0.61	0.72	0.02	0.02	0.01	0.73	0.00	0.03
<i>b</i>	21.36	19.96	18.88	18.09	17.47	16.92	16.52	14.52	13.80	12.90	11.74	10.66	9.20
Δb (s. dev.)	1.01	0.95	1.03	1.01	1.02	1.07	1.17	0.03	0.01	0.01	0.25	0.01	0.03
Orange juice													
<i>N</i>	6	6	6	6	6	6	3	3					
<i>L</i>	40.23	46.40	50.08	52.28	53.19	53.21	53.35	52.31					
ΔL (s. dev.)	2.89	2.23	1.70	1.39	1.35	1.71	2.46	2.73					
<i>a</i>	9.58	8.07	6.53	4.80	3.13	1.53	0.25	-1.37					
Δa (s. dev.)	1.52	1.45	1.25	1.04	0.84	0.46	0.30	0.32					
<i>b</i>	25.24	28.65	30.45	31.17	31.24	30.70	30.44	29.05					
Δb (s. dev.)	1.66	1.21	0.98	1.00	1.20	1.59	1.64	1.77					

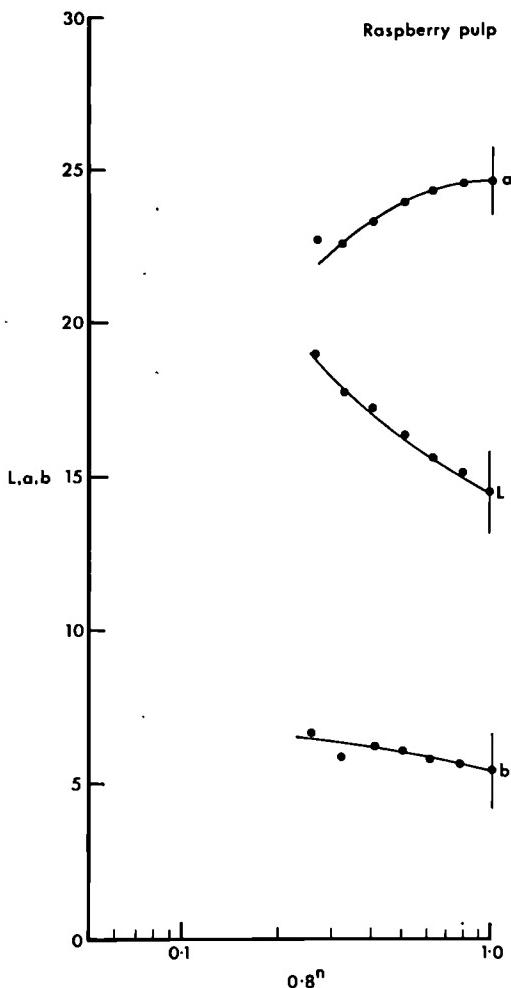


Fig. 5. As Fig. 4 but for raspberry pulp and only overall mean values plotted.

sample 1 are represented in Fig. 7. A histogram type of presentation is adopted because each sample has a particle size range, not a single particle size. This is indicated by the arrows on the figure. Those for the fraction of particle size greater than 1000 μm are extended to show the unknown extent of the distribution. They show some change in the value of L with particle size range but differ in several respects from the results published by Berghaller *et al.* (1983). However, comparing those earlier data with Table 7,

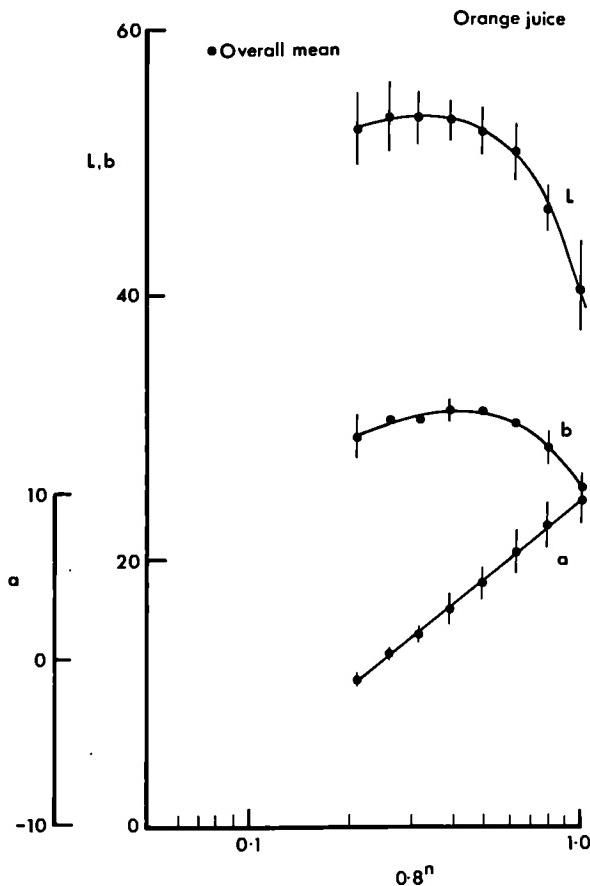


Fig. 6. As Fig. 5 but for orange juice.

which contains the results from one laboratory investigating the effect of aperture size, a close resemblance is seen between those results and these results with the smallest aperture (10 mm). As the particle size decreased, L increased. This is a well-known phenomenon: even intensely-coloured materials appear lighter in colour when finely powdered. Under such circumstances more light is captured by the detector due to the increased number of randomly-orientated reflecting surfaces and the smaller penetration depth of the light into the sample.

Aperture size has only a small effect with these samples, but both a and b tend to become less dependent on particle size as the aperture size is

TABLE 6
MEAN Hunter L, a, b VALUES FOR POTATO POWDERS OF DIFFERENT PARTICLE SIZE RANGES (ALL LABS)

Size range (μm)	< 250	> 250	> 500	> 670	> 1000
Number of labs	6	5	6	6	6
Sample 1					
L	89.37	82.61	78.88	76.19	71.76
ΔL (s. dev.)	0.91	0.77	0.89	0.89	0.98
a	-2.57	-2.98	-2.87	-2.42	-1.35
Δa (s. dev.)	0.53	0.72	0.88	0.79	0.99
b	16.80	22.81	26.74	27.81	29.32
Δb (s. dev.)	1.01	2.12	1.74	0.89	1.38
Sample 2					
L	89.87	84.07	80.60	78.23	74.01
ΔL (s. dev.)	0.68	0.88	0.81	0.89	1.14
a	-1.63	-1.60	-1.67	-1.50	-0.90
Δa (s. dev.)	0.58	0.75	0.83	0.81	0.94
b	12.47	16.78	18.94	19.84	21.03
Δb (s. dev.)	0.27	0.85	1.04	1.16	1.39

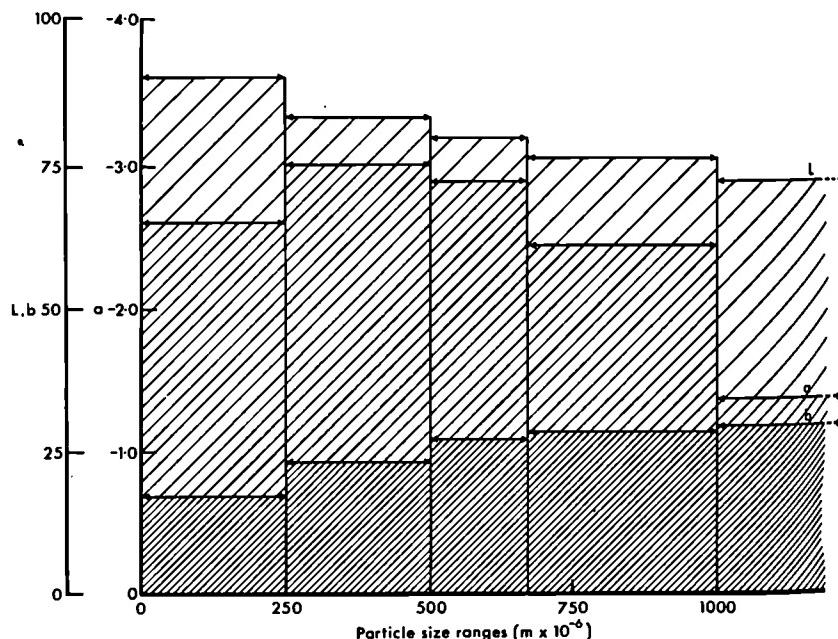


Fig. 7. Hunter L, a, b values for potato powders of different size distributions. The particle size distributions are indicated by the horizontal arrows.

TABLE 7

EFFECT OF PARTICLE SIZE RANGE AND INSTRUMENT APERTURE DIAMETER ON THE HUNTER L , a , b VALUES FOR POTATO POWDERS (RESULTS FROM ONE LABORATORY ONLY)

Size range (μm)	< 250	> 250	> 500	> 670	> 1000
Sample 1					
Aperture size 50 mm					
L	88.60	81.56	77.91	75.28	71.08
ΔL (s. dev.)	0.14	0.04	0.17	0.10	0.75
a	-2.61	-4.00	-3.51	-3.01	-2.22
Δa (s. dev.)	0.02	0.05	0.03	0.06	0.15
b	16.33	26.22	27.63	28.15	29.95
Δb (s. dev.)	0.20	0.18	0.09	0.01	0.22
Aperture size 25 mm					
L	89.54	81.10	76.92	73.97	69.47
ΔL (s. dev.)	0.20	0.20	0.22	0.20	0.76
a	-2.80	-4.02	-3.71	-3.22	-2.43
Δa (s. dev.)	0.16	0.06	0.01	0.05	0.18
b	13.58	25.97	27.05	27.18	28.45
Δb (s. dev.)	0.20	0.14	0.08	0.14	0.11
Aperture size 20 mm					
L	88.85	80.62	76.28	73.44	67.73
ΔL (s. dev.)	0.05	0.13	0.36	0.19	0.86
a	-2.89	-4.07	-3.72	-3.41	-2.49
Δa (s. dev.)	0.04	0.08	0.36	0.19	0.86
b	14.92	25.47	26.62	26.80	27.48
Δb (s. dev.)	0.07	0.09	0.18	0.06	0.27
Aperture size 10 mm					
L	87.50	78.47	73.03	69.31	63.30
ΔL (s. dev.)	0.44	0.19	0.19	0.21	1.71
a	-2.07	-4.29	-4.19	-3.96	-3.26
Δa (s. dev.)	0.04	0.22	0.19	0.11	0.59
b	14.17	23.74	24.59	24.51	23.17
Δb (s. dev.)	0.34	0.08	0.56	0.27	0.45
Sample 2					
Aperture size 50 mm					
L	89.42	83.19	79.92	77.29	83.24
ΔL (s. dev.)	0.20	0.14	0.12	0.21	0.46
a	-1.53	-2.30	-2.29	-2.05	-1.60
Δa (s. dev.)	0.15	0.05	0.02	0.05	0.08
b	12.18	17.45	19.15	19.92	21.23
Δb (s. dev.)	0.05	0.12	0.05	0.08	0.21

(continued)

TABLE 7—*continued*

Size range (μm)	< 250	> 250	> 500	> 670	> 1000
Aperture size 25 mm					
<i>L</i>	90.27	82.65	79.12	76.26	70.98
ΔL (s. dev.)	0.10	0.08	0.17	0.42	1.30
<i>a</i>	-1.82	-2.36	-2.38	-2.12	-1.61
Δa (s. dev.)	0.11	0.03	0.08	0.06	0.17
<i>b</i>	10.32	16.94	18.63	19.07	20.21
Δb (s. dev.)	0.08	0.07	0.04	0.14	0.32
Aperture size 20 mm					
<i>L</i>	89.00	82.46	78.15	75.55	69.96
ΔL (s. dev.)	0.42	0.14	0.08	0.36	0.12
<i>a</i>	-2.11	-2.48	-2.39	-2.39	-1.95
Δa (s. dev.)	0.04	0.01	0.03	0.14	0.17
<i>b</i>	11.98	16.77	18.26	18.96	19.45
Δb (s. dev.)	0.44	0.10	0.04	0.09	0.14
Aperture size 10 mm					
<i>L</i>	88.37	80.18	75.04	70.84	65.18
ΔL (s. dev.)	0.38	0.34	0.07	1.17	1.28
<i>a</i>	-2.09	-2.57	-2.79	-2.68	-2.16
Δa (s. dev.)	0.14	0.20	0.11	0.15	0.10
<i>b</i>	11.16	15.59	16.45	16.69	16.66
Δb (s. dev.)	0.38	0.23	0.11	0.23	0.47

decreased. For *L* the reverse is the case, the difference in *L* values at different particle sizes increasing with decreasing aperture size.

One further anomaly evident is that as the particle size is reduced, *a* increases until the particles are less than 250 μm when *a* begins to decrease. However, *a* is small and the differences observed between each range of particle size are in general smaller than the between-laboratories standard deviation. It is only the observation that this behaviour was experienced in all laboratories and with both samples which confirms it as a real phenomenon.

(b) Paprika or powdered red pepper

The only results available from this study on this particular product are from one laboratory. These are presented in Table 8. The limited range of mean particle size limits the conclusions to be drawn from these results but

TABLE 8
Hunter L, a, b VALUES FOR PAPRIKA SAMPLES OF DIFFERENT MEAN
PARTICLE SIZE AND DIFFERENT INSTRUMENT APERTURE DIAMETERS
(RESULTS FROM ONE LABORATORY ONLY)

<i>Mean particle size</i> (μm)	<i>0.26</i>	<i>0.18</i>	<i>0.1425</i>
Aperture size 50 mm			
<i>L</i>	33.38	34.40	35.21
ΔL (s. dev.)	0.23	0.39	0.74
<i>a</i>	28.36	28.05	27.82
Δa (s. dev.)	0.14	0.26	0.38
<i>b</i>	19.09	19.66	19.97
Δb (s. dev.)	0.16	0.22	0.44
Aperture size 25 mm			
<i>L</i>	34.36	34.68	36.10
ΔL (s. dev.)	0.17	0.17	0.12
<i>a</i>	27.75	27.53	26.94
Δa (s. dev.)	0.05	0.06	0.34
<i>b</i>	19.49	19.57	20.71
Δb (s. dev.)	0.12	0.12	0.11
Aperture size 20 mm			
<i>L</i>	34.15	34.72	34.56
ΔL (s. dev.)	0.17	0.16	0.26
<i>a</i>	27.96	27.98	27.62
Δa (s. dev.)	0.02	0.18	0.28
<i>b</i>	19.40	19.62	19.49
Δb (s. dev.)	0.10	0.15	0.11

little, if any, effect of aperture size or even of particle size is evident apart from a slight suggestion that *L* increased with decreasing particle size, as is to be expected.

CONCLUSIONS

When results from different laboratories are to be compared, then the measurement method must be carefully standardised. This is clear not only from this work and the results reported in Chapter 22 but also from the collaborative trials conducted in other fields of colour measurement.

Standardisation of the instrument characteristics is, however, only one aspect of this study. One other must be in the specification of the product or, to quote a term used frequently in COST 90bis, *contextualisation* of the data. Thus composition, configuration and many other characteristics of the foodstuff itself may be significant. In the case of the liquids investigated, clearly the concentration is an important factor, as is, in the case of the powdered foods, the particle size. All such factors are potential sources of variation between laboratories and in other chapters further aspects of these problems are discussed.

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DISCUSSION

H. Tijskens asked if aperture-size changes were always free from other concomitant changes in the conditions of measurement, e.g. was the inside of the aperture always the same colour, black? *M. Kent* confirmed that that was so and that in any case the instrument was always recalibrated with each change of aperture. But everything else did remain the same.

Measurement of Tomato Paste Colour: Investigation of Some Method Variables

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SUMMARY

One important use for food colour measurement is in the provision of buying criteria for certain materials. In this situation it is essential that standard methodology has to be agreed and then utilised by both buyer and seller. A commodity which is purchased in large quantities from European producers on the basis of colour quality is tomato paste. There is currently no common standard method used across Europe for its colour measurement and this paper describes work carried out with the aim of establishing such a method. The method is based on the use of a tristimulus colorimeter together with a defined reference tomato-red tile, employed as a 'hitching-post'. The effects of a number of variables which can influence the final colour readings have been examined, including the degree of paste dilution, the test duration, the instrument's aperture size and illumination area, the temperature, the presence of extraneous light and the condition of the reference standard itself.

INTRODUCTION

Colour Control and Measurement of Foods

The initial quality judgement made by a consumer on a food, whether it be at the time of purchase if the food is retailed in a transparent pack or at the time of opening an opaque pack, involves an assessment of various appearance attributes. These attributes include not only colour but also properties such as gloss, surface structure and consistency, component arrangement and pattern, and overall shape, which may be more or less relevant depending on the food. The consumer, through conditioning and

association, expects, even before tasting it, that a food of a certain shape and colour will have particular characteristics in terms of flavour, aroma and texture. The importance of this expectation is well illustrated by the results of a recent consumer study,¹ in which American housewives were asked to define quality in food products. A 'good colour' or 'good appearance' was mentioned more often than, for example, 'tastes good', 'is nutritious', 'has no additives' or 'has a good texture'. As Pangborn² states, colour 'serves as an instant indicator of good or bad, according to the product and its intended use'.

The food industry uses colour measurement and control in relation to foods for a number of reasons. Firstly, there is the need to ensure a standard colour quality. The consumer expects to see a constant colour from unit to unit of a branded product, particularly when the product is packed in transparent containers fully on view on the supermarket shelf. In the case of products unwrapped in the home, colour memory becomes an additional factor in the assessment of colour quality but even so the range of allowed tolerance around the norm is not usually wide. A second use for colour measurement is in the development of new foods or improved versions of existing foods, in cases where the colour is one of the major quality attributes. This is mainly applicable to value-added or manufactured products where there is scope to improve product appeal by optimising manufacturing methods or by incorporating newly available colour-imparting ingredients in the recipes. A third use for measurement of colour of foods is in providing buying criteria for certain raw materials or commodity items. Good examples of this application are in the purchase of tomato paste or citrus juices, where colour is an indication both of original fruit quality and of processing characteristics.

There are obvious differences between the first two applications and the third in the colour measurement methodology. The requirements of the first two applications are usually satisfied by in-house methods, the only proviso being that these should be capable of giving results which can ultimately be used to predict the views of the consumer. Colour difference methods are usually sufficient, the colour of the sample being compared with that of a standard, which might be a quality control norm, or a development sample prepared to a standard recipe or process. On the other hand, the commercial implications of the third application mean that methodology has to be agreed at least between the buyer and the seller, and that colour difference methods can only be used provided there exists a colour standard agreed between the two parties. A great degree of standardisation of and conformity with the methodology is then necessary

in order to reduce the risks of commercial arguments. The alternative to difference meters and agreed standards is absolute colour measurement but this is a technique not well satisfied currently by instrument manufacturers and the available instrumentation is very expensive.

One example of a material which is purchased in large commercial quantities on the basis of colour quality is tomato paste. In 1985 approximately 775 000 tonnes of tomato paste (of equivalent concentration 28/30% solids) were produced in Europe (Italy, Greece, Portugal, Spain and France) from approximately 4·8 million tonnes of fresh fruit,³ and this accounted for almost 60% of the world production in paste. Assuming an approximate price of 700 ecu per tonne, this amount had a value of 543 million ecu (£387 million). Approximately 35% was exported outside the European Community.

Tomato Colour

The tomato is one of the best examples of a food which possesses intense natural colour and which is then capable of imparting this colour to a wide range of products. Colour is thus a major quality attribute of tomatoes and processed tomato products, including tomato paste and tomato purée. Indeed these products have probably received more colour research than any other single food group. This is for two reasons, firstly because the colour of the raw tomato is an index of maturity and this in turn is related to maximum flavour development, and secondly because the colour is also affected by the processing conditions.

The characteristic red colour of tomato is due to a combination of carotenoid pigments, of which the most abundant is lycopene, comprising about 83% of the pigments present. The balance may be composed of α -, β -, γ - and δ -carotenes and xanthophylls. Watada *et al.*⁴ have related the loss of green chlorophyll content and increase of carotenoid pigment content to progress of ripening. Other workers⁵⁻⁷ have noted the effect of various climatic and other conditions on pigment formation. Pigment intensity is much greater in vine-ripened fruit grown outside under summer conditions, especially if the fruit is harvested at the middle of the season. However, very high ripening temperatures cause a decrease in colour. Fruit grown at the beginning or end of the season, greenhouse-ripened fruit or fruit picked green and ripened in storage are known to have a lower carotenoid content and are, in consequence, of lower colour intensity. Excess nitrogen in the soil, though it increases yields, is said to decrease pigmentation but phosphorus and potassium in the soil have the reverse effect. Certain varieties of tomato naturally have more pigment than others.

The colour of tomato products, such as pastes and purées, is related to that of the original fruit but is also a function of the processing conditions.⁸ It has been said that a poor-colour tomato cannot be improved by regulation of the process but that a good-colour fruit may easily be ruined by poor processing conditions. Improvements in processing technology, such as the gradual replacement of batch-type concentrators (Boules) by continuous concentrators; the increase in the efficiency of continuous concentrators by use of triple or even quadruple effect evaporation, the use of short residence-time 'breaking' equipment such as the super hot break or even super-super hot break plant and the use of more efficient cooling equipment coupled with aseptic filling of containers, have all led to a dramatic improvement in processed tomato product colour over the last decade.

The colour of tomato pastes is therefore important not only because it influences the appearance of the final product such as soups, juices, ketchups, etc., but also because it serves as an indicator of the quality of the original tomatoes, the efficiency of the processing conditions and the adequacy of the quality control in the paste-producing factory. It is not surprising that colour measuring systems have been developed for tomato products on both a company and a national scale.

Pioneering work carried out by MacGillivray⁹ in the US resulted in the first national colour scoring system for tomatoes and tomato products, adopted for use by the USDA in 1938. In the MacGillivray system scores were assigned to samples by comparing them to colours produced by spinning discs prepared from coloured papers supplied by the Munsell company (the spinning disc colorimeter). This system is still in wide use, but in 1977 and 1978 the USDA published amendments to the USDA standards for grades of tomato paste and other tomato products which would permit instrumental evaluation of their colour. These amendments resulted from exhaustive collaborative trials¹⁰ carried out between workers at the University of California in Davis, the USDA, the California Canners' League and various instrument manufacturers. The Canners' League currently allows the use of Hunter, Agtron and Gardner instruments, and equations for conversion of instrumental results to comparable USDA colour scores have been evolved. Alternatively, many suppliers and purchasers of tomato products use Judd-Hunter L , a and b values or simple derivations from these values, such as the a/b ratio or $a/L\sqrt{(a^2 + b^2)}$. This latter formula, due to Yeatman *et al.*,¹¹ is known as the TC index (tomato colour index). It is interesting to note that two of the instruments approved by the USDA are tristimulus types, the Hunter and the Gardner, whilst the

third is a simple two-point reflectance device based on the spectral curve of tomato. Reflectance at 640 and 546 nm is measured.

The study reported below describes part of the work carried out either in the COST programme or in the author's laboratory relating to the establishment of a standard procedure for the measurement of tomato paste colour, including the defining of a standard tomato-red coloured tile on which the procedure depends. Such a procedure and colour tile could form a standard method which could be used by European producers and users of tomato paste. In view of the US experience with tristimulus colorimeters, and the fact that many European tomato paste producers and purchasers already possess tristimulus colorimeters, it was decided at the outset of the study to investigate the use of this type of instrumentation for this particular application.

Methodology for Colour Measurement

A typical method for measuring tomato paste colour using a tristimulus colorimeter would be as follows:

1. Standardise the instrument using a red standard which has previously been calibrated against a master standard, and a black tile for the zero reading. The standard can be either a dry standard such as a ceramic or enamel tile or a wet standard such as a precalibrated tomato paste. A glass plate should be interposed between the instrument port and the colour standard. The aperture for standardisation is defined.
2. Dilute the paste to a defined TSS (tomato soluble solids by refractometer) with deaerated water at a defined temperature.
3. Transfer a fixed volume of the diluted paste to a sample cup, the base of which is made of the same optically-clear glass and is the same thickness as the plate used in step 1 above.
4. Place the sample cup over the aperture of the instrument, such that the sample is illuminated from below, and place an opaque black cover over the sample cup. The aperture size is defined.
5. Determine the colour values as L, a, b readings, in terms of 45–0° or 0–45° viewing geometry, using CIE illuminant C and 2° observer, with specular reflectance excluded.

As can be seen there are a number of variables which can affect the final result and which require tighter specification in order to achieve a method which could serve as a European standard method. Some of these variables

have been investigated during the COST programme (see Chapters 22, 23 and 25) and others have been studied at the author's laboratory. These variables include:

- The TSS of the diluted paste.
- The aperture size.
- The illuminated area size.
- The colour standard used for instrument calibration.
- The test temperature.
- The time during which the sample is measured.
- The presence or absence of a glass plate during calibration.
- The presence or absence of a black cover during sample measurement.

EXPERIMENTAL

1. The TSS of the Diluted Paste

The reason for diluting tomato paste is because there are a multiplicity of concentrations available from the suppliers, ranging from 20% up to 46% TSS, and for comparative purposes they should all be measured at the same concentration.

The USDA method requires a dilution to 8·5% NTSS ('natural tomato soluble solids'), for historical reasons associated with the fact that the soluble solids of American tomato juice is in this region and it was logical to dilute to the same solids as that of the most successful product manufactured from the paste. In Europe this logic does not apply because other products are sold in greater quantities than tomato juice (baked beans, tomato soups, ketchup).

In order to ascertain the importance of the dilution factor, the following procedure was carried out.

The contents of a number of 5 kg cans of tomato paste (36/38% TSS) from the same source of supply and date of manufacture were bulked together and efficiently mixed under vacuum with sufficient water to reduce the TSS to 30% and sufficient sorbic acid to achieve a concentration of 2000 mg kg⁻¹ at this dilution. The paste was then transferred to cans with plain tinplate bodies and lacquered ends (300 × 207 UT) and the cans were closed. The cans were stored refrigerated until required for testing. The contents of a can were then diluted from 30% TSS to 25%, 20%, 15%, 12%, 10% and 8% TSS, and colour measurements were then made at each dilution using the method given in Appendix A, except that the 'hitching-post' was a red paper from the Swedish National Standard colour atlas

(Ref. NCS 5050 Y80R) assigned the colour values $L = 25.16$, $a = 26.00$ and $b = 13.14$. (See Chapter 23 for a full account.)

2 The Aperture Size and Illuminated Area

Hunter and Christie¹² have advised that for highly coloured translucent samples it is preferable to use a large aperture size but a small illuminated area. This is in order to capture that proportion of the light scattered by the sample and then returned to the detector from outside the area illuminated.

The L , a and b values and a/b ratio of the paste used in Experiment 1 were determined using various combinations of Hunterlab Labscan aperture size (between 50 and 10 mm) and illumination area (between 44 and 6 mm) at different dilutions of paste. The method used is that in Appendix A, except that the 'hitching-post' was the red paper from the Swedish National Standard colour atlas identified earlier.

3 'Hitching-post' Colour Reference

The advantages of the 'hitching-post' technique, where an instrument is standardised on a calibrated standard of a colour as close as possible to that of the specimens to be measured, have been stressed in many instrument manuals for colour difference meters. Hitching-posts can help in two ways: to reduce the effects of long-term drifting of a particular instrument and to improve instrument-to-instrument repeatability. Some results from the COST project serve to illustrate the second reason. The experiment outlined in Experiment 1 above was repeated, except that the initial instrument standardisation was carried out with standard black and white tiles rather than the black tile and the red paper from the Swedish colour atlas (Chapter 23).

4 The Test Temperature

Both the tomato tile used as a hitching-post during calibration and tomato paste itself are thermochromic, i.e. their colour values change as the temperature changes. Malkin¹³ has suggested that thermochromicity always appears to be associated with a steep portion in the spectral plot of a sample. Tomato paste and tomato tiles show steep portions in their spectral curves in the region around 630 nm (see Fig. 1).

Some experiments carried out in the author's laboratory demonstrate the effect and extent of the thermochromicity of tomato paste and a tomato tile. A typical tomato paste was diluted to 12% TSS and then held at various temperatures from 10 to 40°C prior to measurement. Measurements were then carried out using a Hunterlab Labscan calibrated on black and white

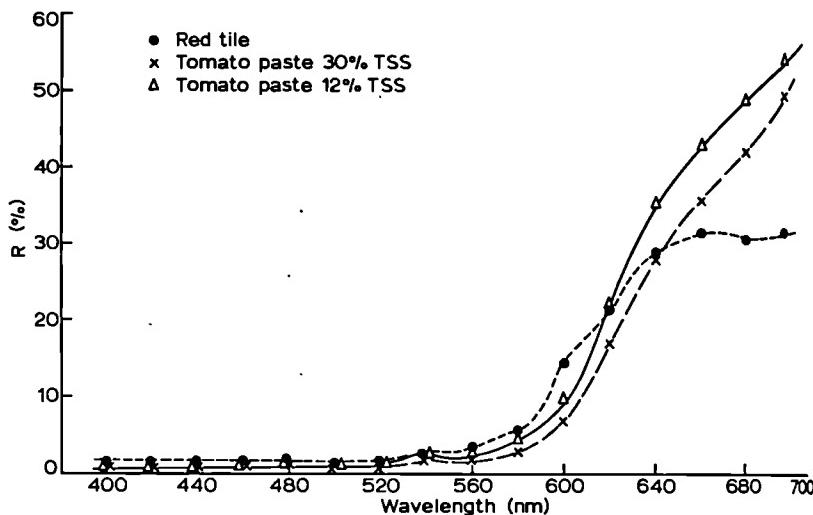


Fig. 1. Tomato spectral reflectance data.

tiles. In another experiment an enamel tomato tile was held at different temperatures and then measured on the colorimeter calibrated on black and white. Finally, the effect of measuring a paste held at different temperatures, 'hitching' to a red tile held at the same temperatures, was also tested. Except for these variations, the method followed was in all cases as in Appendix A.

5. Duration of the Test

A very simple experiment carried out in the author's laboratory illustrates the importance of not allowing the sample to remain in the sample cup for long periods before colour measurement. A typical tomato paste was diluted to 12·0% TSS and 8·0% TSS and samples transferred to the sample cups. The sample cups were allowed to stand for various time intervals before carrying out colour measurements using the method given in Appendix A.

6. Presence of Glass Plate During Instrument Standardisation

A number of instrument manufacturers advocate the use of a glass plate between the instrument port and the black reference tile or the hitching-post reference tile during the standardisation procedure, the glass plate being dimensionally and optically identical to the glass forming the base of

the sample container. Some preliminary data are available from work carried out in the author's laboratory, examining the effect of omitting this stage from the standardisation method.

The colour values of some typical tomato pastes were measured using the procedure given in Appendix A and the measurements were then repeated omitting the glass plate.

1. Presence of Black Cover During a Test

The USDA method for tomato colour measurement using tristimulus colorimeters advocates the use of a black cover around the sample to eliminate the effect of extraneous light, particularly with dilute samples. The effect of including or excluding the black cover on the colour values of the tomato paste prepared in Experiment 1, at two dilutions and two aperture/illumination area combinations, was assessed in one laboratory using the method given in Appendix A. In order to gain data on within-laboratory variances, the procedure was replicated a number of times on the same sample.

In a second experiment the effect on the colour values of a typical tomato paste measured using various aperture/illumination combinations in conjunction with the presence or absence of the black cover was assessed in more depth but without replication. Again the method of Appendix A was used.

RESULTS

1. The TSS of the Diluted Paste

The results of the experiment (see Fig. 2, Table 1) show the effects of dilution on the L , a , b values and a/b ratio. Dilution of the paste causes a rise in the L value, a fall in the a value and a slight rise in the b value. The a/b ratio therefore falls as the soluble solids fall and there is apparently a linear relationship between these two factors. Extensive work carried out in the author's laboratory using a large number of pastes from different sources has indicated that between TSS levels of 10 and 30% the change in a/b ratio is on average 0.013 a/b units per 1% TSS. Below 8–10% TSS there is a more rapid decrease in a value and even a fall in b value which results in a departure from linearity of the a/b ratio versus TSS relationship. The departure from linearity is in such a direction that any errors in making the dilution would result in a greater change in a value or a/b ratio than in the linear region. The importance of not only strictly defining the dilution value

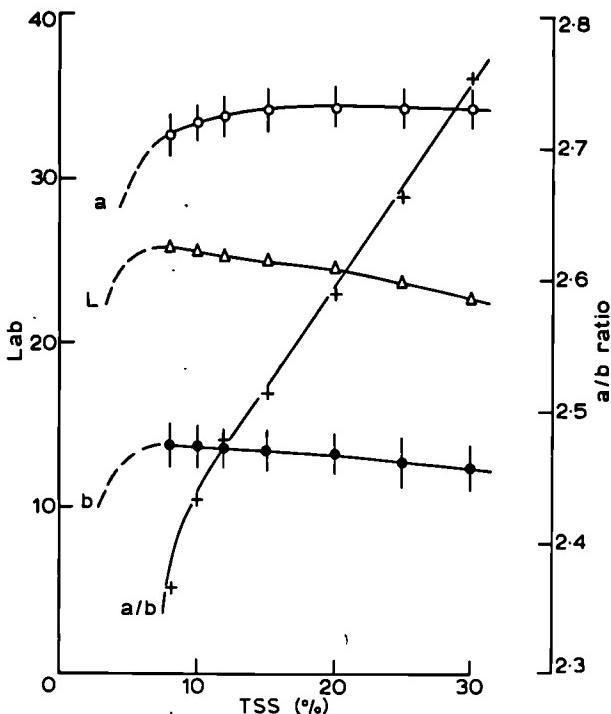


Fig. 2. Effect of dilution on colour values.

but also of working at a higher value than 8.5% TSS is well illustrated by the results.

The Aperture Size and Illuminated Area

The effect of illuminated area and aperture size on colour values is demonstrated by the data given in Fig. 3(a-d) (giving L , a , b and a/b values, respectively).

The effect of aperture is more pronounced than the effect of illumination area and this is particularly true in the case of the a value. Decrease of aperture at constant illumination area causes a large decrease in the a value but the b and L values also decrease. The large decrease in the a value gives a corresponding large decrease in the a/b ratio. These effects are most marked at the lower concentrations.

A decrease in illumination area at constant aperture, on the other hand, gives a slight increase in a , b and L values. This is in line with Hunter's

recommendations to use large apertures and small illumination areas. The increases in a and b values result, however, in very little change of the a/b ratio.

In the dilution experiment described under Experiment 1, a number of laboratories submitted additional results at different instrumental aperture and illumination settings from those advised (50 mm, 50 mm). It was possible to extract results at the same aperture/illumination ratio (i.e. 1:1) for aperture sizes from 50 mm down to 8 mm. These results are plotted in Fig. 4 at two dilutions, 8% and 12% TSS. A decrease in aperture and illumination area, keeping the ratio at 1:1, causes a decrease in a , b and L values and a decrease in a/b ratio.

'Hitching-post' Colour Reference

Colour values and between-laboratory variances for tomato pastes measured with and without a hitching-post are given in Table 1. Standard deviations are similar except in the important case of the a values, where the variances are much smaller when the hitching-post method is used. The advantages of this technique are demonstrated (see also Chapter 23).

TABLE 1
EFFECT OF DILUTION OF TOMATO PASTE ON COLOUR VALUES

% TSS	Number of laboratories	<i>L</i>		<i>a</i>		<i>b</i>		<i>a/b</i> ratio
		Value	S.D.	Value	S.D.	Value	S.D.	
Hitching-post measurement								
30	7	22.86	0.409	34.12	1.23	12.40	1.56	2.75
25	7	23.87	0.375	34.31	1.24	12.90	1.42	2.66
20	7	24.54	0.488	34.29	1.14	13.23	1.39	2.59
15	7	24.99	0.488	34.16	1.27	13.57	1.35	2.52
12	7	25.37	0.511	33.78	1.33	13.68	1.26	2.47
10	7	25.59	0.580	33.40	1.41	13.75	1.23	2.43
8	7	25.76	0.505	32.77	1.28	13.87	1.25	2.36
Absolute measurement								
30	6	22.74	0.353	33.98	3.06	12.13	1.24	2.80
25	6	23.70	0.432	34.01	2.71	12.78	1.22	2.66
20	6	24.23	0.322	34.09	2.59	13.02	1.23	2.62
15	6	24.79	0.330	34.04	2.59	13.31	1.10	2.56
12	7	25.14	0.291	33.71	2.50	13.51	1.09	2.50
10	6	25.34	0.302	33.19	2.79	13.54	0.53	2.45
8	6	25.51	0.419	32.56	1.41	14.01	1.35	2.32

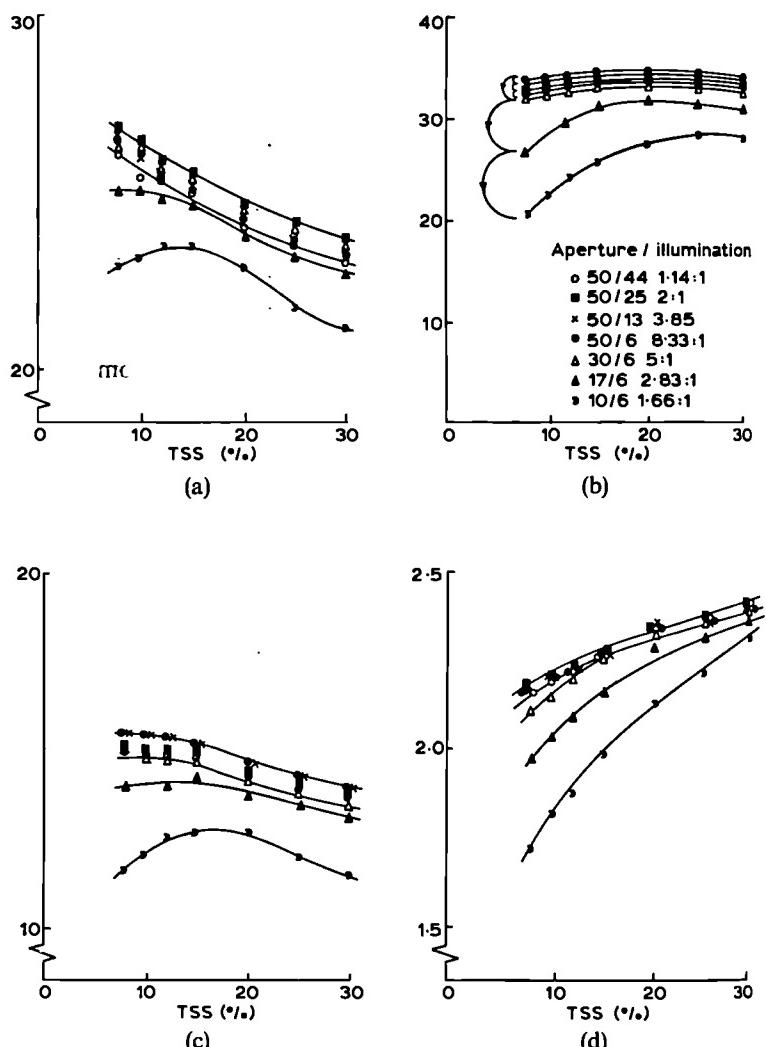


Fig. 3. Effects of aperture size and illumination area on colour values. (a) L^* value; (b) a^* value; (c) b^* value; (d) a/b ratio.

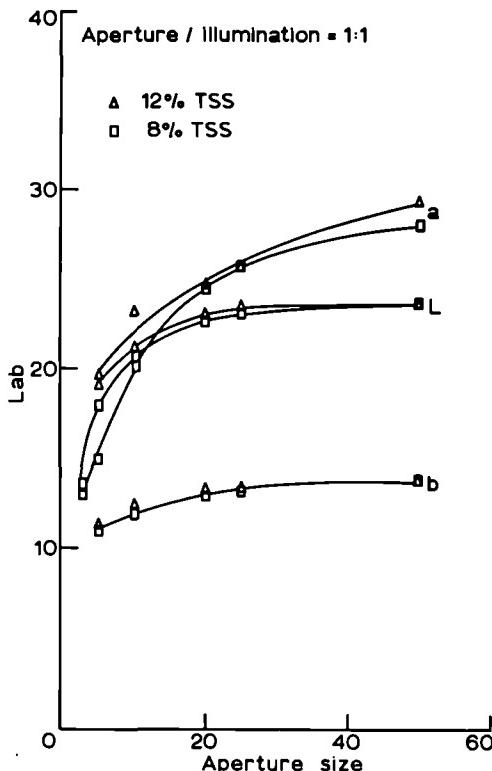


Fig. 4. Effect of aperture on colour values at $A/I = 1:1$.

The Test Temperature

Results of this experiment are given in Table 2(a,b,c). The thermochromicity of tomato paste (Table 2a) is approximately $0.047 \Delta E/^\circ\text{C}$ (where $\Delta E = [(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2]^{1/2}$) whereas for the tomato tile (Table 2b) it is $0.054 \Delta E/^\circ\text{C}$. In both cases there are trends in the colour values with change of temperature. For the tile there is a decrease in L , a and b values with temperature rise. For the tomato paste there is little effect on L values but a rise in a and b values. The different effects of temperature on tile and paste may be due to other factors affecting colour such as chemical reactions occurring in the paste, accelerated at higher temperatures. Table 2c gives results from an experiment simulating a possible real-life situation in which a testing laboratory may not be equipped with temperature-controlled cabinets for maintaining the temperature of tiles or

TABLE 2

(a) EFFECT OF TEMPERATURE ON TOMATO PASTE COLOUR VALUES
 (after instrument standardisation on black and white tiles;
 Hunterlab Labscan; $A/I = 50/44$ mm)

<i>Sample temperature</i> (°C)	<i>L</i>	<i>a</i>	<i>b</i>	<i>a/b</i> <i>ratio</i>
10	23.34	30.10	13.57	2.22
15	23.30	30.41	13.71	2.22
20	23.38	30.40	13.67	2.22
25	23.42	30.54	13.74	2.22
30	23.41	30.76	13.83	2.22
35	23.58	31.11	13.92	2.23
40	23.59	31.27	13.97	2.24

(b) EFFECT OF TEMPERATURE ON TOMATO TILE COLOUR VALUES
 (conditions as Table 2a)

<i>Tile temperature</i> (°C)	<i>L</i>	<i>a</i>	<i>b</i>	<i>a/b</i> <i>ratio</i>
10	26.15	29.46	12.84	2.29
15	26.06	29.20	12.69	2.30
20	25.98	28.92	12.51	2.31
25	25.85	28.77	12.42	2.32
30	25.74	28.60	12.29	2.33
35	25.62	28.42	12.17	2.34
40	25.47	28.26	12.06	2.34

(c) EFFECT OF TEMPERATURE ON TOMATO PASTE COLOUR VALUES WHEN HITCHING TO A
 TOMATO TILE AT THE SAME TEMPERATURE
 (conditions as Table 2a)

<i>Sample temperature</i> (°C)	<i>Tile temperature</i> (°C)	<i>L</i>	<i>a</i>	<i>b</i>	<i>a/b</i> <i>ratio</i>
10	10	23.01	29.82	13.27	2.25
15	15	23.06	29.92	13.30	2.25
20	20	23.19	30.39	13.42	2.26
25	25	23.20	30.39	13.50	2.25
30	30	23.26	30.62	13.61	2.25
35	35	23.64	31.33	13.83	2.27
40	40	23.64	31.34	13.85	2.26

TABLE 3
EFFECT OF DURATION OF TEST ON COLOUR VALUES OF TOMATO PASTE AT TWO
DILUTIONS

<i>Time</i> (min)	<i>L</i>	<i>a</i>	<i>b</i>	<i>a/b</i>	ΔE reference (0 min)
Paste diluted to 12% TSS					
0	23.05	29.78	13.23	2.25	—
15	23.01	29.76	13.23	2.25	0.045
30	23.00	29.80	13.24	2.25	0.055
60	22.99	29.83	13.25	2.25	0.081
120	22.99	29.92	13.25	2.26	0.154
Paste diluted to 8% TSS					
0	23.51	29.37	13.42	2.19	—
15	23.49	29.32	13.40	2.19	0.057
30	23.45	29.41	13.40	2.19	0.075
60	23.39	29.47	13.42	2.19	0.156
120	23.36	29.57	13.43	2.20	0.250

samples at 20°C. In this case it would be likely that tile and sample would both be at the ambient temperature of the laboratory. It can be seen that there are still trends in *a*, *b* and *L* values in that they all increase with increase of temperature. Interestingly the effects on *a/b* ratio are, however, negligible.

The Duration of the Test

It can be seen (Table 3) that even at 12.0% TSS there are changes in colour values with time. The changes are more marked at 8.0% TSS. As expected, the trends are to an increase in *a* value and decrease in *L* value. It would be expected that, with pastes of lower viscosity, the *a* value and therefore the *a/b* ratio would increase more rapidly with time, due to settling of tomato fibres to the base of the sample cup. The same problem has been noted by Kent with raspberry pulps (Chapter 23).

The Glass Plate During Instrument Standardisation

The results in Table 4 indicate that the glass plate has a large influence on the tomato paste colour values determined. All three *L*, *a*, *b* colour values are reduced if during the standardisation stage the glass is not present between the black and hitching-post tiles. The percentage reduction is similar in each case (around 4.5%), which results in the *a/b* values, with or

TABLE 4
EFFECT ON TOMATO PASTE COLOUR VALUES OF STANDARDISING WITHOUT THE GLASS PLATE

<i>Sample number</i>		<i>L</i>	<i>a</i>	<i>b</i>	<i>a/b</i>	ΔE
1	With glass	26.21	29.91	14.55	2.06	—
	Without glass	24.80	28.58	13.80	2.07	2.078
2	With glass	25.01	33.00	14.25	2.32	—
	Without glass	23.60	31.58	13.57	2.33	2.114
3	With glass	24.13	27.62	13.51	2.04	—
	Without glass	22.75	26.66	12.98	2.05	1.763

TABLE 5a
EFFECTS ON COLOUR VALUES OF TOMATO PASTE OF MEASURING WITH OR WITHOUT BLACK COVER

<i>% TSS</i>	<i>Aperture and illumination D (mm)</i>		<i>L</i>	\bar{a}	\bar{b}
20	50	With cover	22.37	28.76	13.07
		Without cover	22.38	28.79	13.07
		Δ	0.013	0.032	0.007
		Significance	**	**	—
25	25	With cover	22.09	26.94	12.85
		Without cover	22.06	27.08	12.84
		Δ	0.023	0.139	0.011
		Significance	***	**	—
11.3	50	With cover	23.45	28.01	13.60
		Without cover	23.47	28.04	13.60
		Δ	0.017	0.030	0.008
		Significance	***	**	—
	25	With cover	23.19	26.07	13.24
		Without cover	23.16	26.20	13.22
		Δ	0.028	0.129	0.015
		Significance	—	*	—

TABLE 5b

EFFECT ON COLOUR VALUES OF TOMATO PASTE OF MEASURING AT DIFFERENT APERTURE/
ILLUMINATION CONDITIONS, WITH OR WITHOUT BLACK COVER

<i>Aperture/ illumination D (mm)</i>		<i>L</i>	<i>a</i>	<i>b</i>	ΔE
50/44	With cover	23.19	29.73	13.28	—
	Without cover	23.08	29.58	13.20	0.203
50/25	With cover	23.52	30.56	13.54	—
	Without cover	23.38	30.34	13.45	0.276
50/13	With cover	23.83	31.21	13.80	—
	Without cover	23.49	30.67	13.54	0.689
50/6	With cover	23.76	31.41	13.90	—
	Without cover	23.38	30.77	13.55	0.823
30/25	With cover	22.64	27.87	12.81	—
	Without cover	22.61	27.81	12.85	0.078
30/13	With cover	23.15	29.44	13.27	—
	Without cover	23.04	29.47	13.26	0.115
30/6	With cover	23.23	29.51	13.27	—
	Without cover	23.14	29.45	13.22	0.119
17/13	With cover	21.96	25.20	12.32	—
	Without cover	21.91	25.23	12.30	0.062
17/6	With cover	22.18	25.73	12.44	—
	Without cover	22.19	25.63	12.46	0.103
10/6	With cover	19.91	19.52	10.67	—
	Without cover	19.95	19.46	10.68	0.073

without the presence of the glass plate, being very similar for a particular sample.

The Presence of the Black Cover During a Test

Table 5a gives the results from the first experiment described in Section 7, involving the within-laboratory replication of the measurements, with and without black cover. The results indicate that there can be a statistically significant within-laboratory difference in colour values between the two conditions, particularly in the cases of the *L* and *a* values. However, these differences are very much smaller than the between-laboratories variances shown in Table 1. It could be suggested on the strength of these results that the presence of the black cover may not be necessary. In Table 5b the effect

of various aperture/illumination combinations as well as presence/absence of black cover is demonstrated. There is evidence that at small diameter illumination settings, in combination with large aperture settings, the differences between the readings with and without black covers approach the interlaboratory differences noted in Table 1. ΔE values are highest at the highest aperture, indicating some influence of the outside lighting conditions. ΔE values increase as the illuminated area decreases at this aperture. The effect of including or excluding the cover has little influence on the final a/b ratio.

It should be mentioned that both these experiments were carried out away from direct sunlight in rooms lit mainly by artificial light, giving approximately 590 lux at bench level. In more brightly-lit conditions, for example on a sun-lit bench at mid-day where the light level may be 60 000 lux or more, the omission of a black cover may have a significant effect.

CONCLUSIONS

During the work described a number of variables of possible significance in the methodology for measurement of tomato paste colour have been identified, and their effects assessed and in some cases quantified. In order to standardise the methodology, most of these variables would need to be controlled and defined. A number of recommendations can be made.

Dilution factor: It is recommended that, for a standard procedure, tomato paste be diluted to a TSS of 12% measured at 20°C on the sugar scale. This concentration coincides, by design, with that used for another important quality test carried out on tomato paste, the Bostwick Consistency test.

Aperture size and illumination area: It is recommended that for a standard method both settings be specified. Aperture settings between 30 and 50 mm would be permissible, as would illumination settings between 6 and 50 mm (provided that illumination setting \leq aperture setting), since differences arising due to these two factors are no greater than experimental errors and instrument-to-instrument repeatability.

Hitching-post: The advisability of using the 'hitching-post' technique for instrument standardisation has been demonstrated and it is recommended that a batch of tomato paste-red glazed ceramic tiles, all having the same or very similar colour values, be made available as a reference standard for use

by European tomato paste suppliers and purchasers. The batch should consist of tiles remaining after discarding those with surface blemishes and those which have colour values differing from the average colour values of the batch by more than a defined amount. The average colour values should be approximately $L = 25$, $a = 32$, $b = 14$ ($a/b = 2.3$) and spectral reflectance data should be similar to that given in Fig. 1 for the diluted tomato paste at 12% TSS. A tile having the average colour values should be calibrated by an accredited standardisation facility, such as the UK National Physical Laboratory (NPL), to become the master standard. The colour values of all the tiles in the batch can then be referred to the master.

Test temperature: It is recommended that, in view of the thermochromicity of tomato paste and tomato tile standards, a test temperature of, say, 20°C be adopted as part of the standard procedure.

Duration of the test: It is recommended that because of sample heating effects under instrument lamps and sample settling effects in test containers colour values be determined within 10 min of sample preparation and within 30 s of placing under the instrument lamp.

Glass plate during standardisation: Further work is required on this but in the meantime it is suggested that, in view of the purely practical problem of breakage of the glass plate in use (a problem which occurs frequently even in the best-run laboratory), the use of the plate be omitted from the procedure.

Black cover: Further work is also required on this aspect but, in view of the variability of laboratory lighting conditions, the black cover should be retained.

Some further work is still required before a standard methodology for the measurement of tomato paste colour can be finalised. This work should include the effects on tomato colour values of the sample depth and sample container diameter, of the thickness of the glass base of the sample container, of the inclusion of the specular component of reflectance in the measurement, and finally of the different Perfect White Diffuser values originated by the different Standards Institutes in different countries. The white diffuser values would be employed during the determination of the master calibration of any red tile standard and it is important that a consensus is achieved between the Standards Institutes on this matter.

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The author is grateful to all the laboratories who contributed data relating to tomato colour measurements, without which the effects of the measurement variables could not have been assessed. In particular, he would like to thank Ms M. Wilsch and her staff at the Londreco Ltd analytical laboratory.

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APPENDIX: METHOD FOR COLOUR MEASUREMENT OF TOMATO PASTE

1. Apparatus and Materials

Suitable tristimulus colorimeter (e.g. Hunterlab D25, Hunterlab Labscan, Gardner XL20).

Standard black, white and tomato tiles, maintained at 20°C.

Pastel tiles as required, maintained at 20°C.

Optically clear glass specimen cell (diameter 2·5 in (62·5 mm), height 2·5 in (62·5 mm)), maintained at 20°C.

Clear glass plate to match optically the specimen cell base (75 × 75 × 2 mm).

Empty tin can, approximately 75 mm internal diameter and 140 mm height, painted matt black internally.

Deaerated distilled water at 20°C.

Abbé-type refractometer with sugar scale (in % TSS).

Balance.

2. Method

(a) Sample preparation

Tomato paste samples for colour measurement must be diluted from their original tomato soluble solids (TSS) to $12\cdot0 \pm 0\cdot1\%$ using distilled water which has been deaerated just prior to use.

(i) Determine the % TSS of the paste by the standard method (mix about 50-g sample with a spatula and allow to come to 20°C, place approximately 10 g of this paste in the middle of a square of film muslin, gather up the corners so as to enclose the sample and squeeze progressively so as to force the serum through the cloth, reject the first few drops, allow two or three drops to fall on to the prism of an Abbé-type refractometer which has also been equilibrated to 20°C; take a reading. Repeat and take the average).

(ii) A net weight of 300-g diluted sample is required. Calculate the amount of undiluted paste (W_p) required to give this from the following equation:

$$W_p = \frac{12}{\% \text{ TSS}} \times 300$$

(iii) Weigh accurately W_p g of paste at 20°C into a 400-ml beaker.

(iv) Add sufficient deaerated distilled water at 20°C to give a total of 300 g. Add the water in small amounts and stir after each addition to minimise problems with lumps. Take care not to entrap air in the mix.

Finally, stir thoroughly and check the % TSS. Adjust with paste or distilled water as necessary.

(b) Colour measurement

Colour values should be determined in terms of 45–0° or 0–45° viewing geometry, illuminant C/2° observer, specular reflectance excluded, referred to a national standard Perfect White Diffuser and expressed in Hunter *L*, *a* and *b* values. The *a/b* ratio can then be calculated as required.

The colorimeter is standardised ready for application of the 'hitching-post' technique in the normal way, as described in the instrument manual. The hitching-post is a tomato-red enamelled tile, unless otherwise stated, which has itself been precalibrated against a master tomato tile. The sample is 'read' through the base of a glass cell using a light shield to prevent ingress of extraneous light.

- (i) The following conditions of illumination and viewing (Table A.1) should be set on each instrument, unless otherwise stated, before carrying out the standardisation and measurement procedures described below.
- (ii) To standardise the colorimeter on zero scale, place a glass plate which optically matches the glass of the cuvette base and is the same thickness over the instrument port. Place the black tile supplied for zero adjustment on the glass plate. Make the zero adjustment as described in the instrument manual. Ensure that both the glass plate and the black tile are free from dust and marks prior to use.
- (iii) To standardise the instrument on the tomato-red 'hitching-post', use the calibrated results on the back of the tile and proceed as for the method of calibration on the white tile standard described in the instrument manual. Make sure that the clear glass plate is in place between the red tile and the aperture whilst carrying out the standardisation, and also that the

TABLE A.1

<i>Illuminant C, 2° (specular reflectance excluded)</i>		
<i>Instrument type</i>	<i>Aperture diameter (mm)</i>	<i>Illuminated area (mm)</i>
Hunterlab D25A-2	51	44
D25M-2	51	51
D25M-PC2	51	51
Labscan	50	44
Gardner XL20	50	50

tile is not allowed to warm up under the lamp whilst at the specimen port. Adjustments should be made as quickly as possible.

(iv) Introduce 170 ml of sample into the sample cell and place on the viewing port (the sample level is approximately 12 mm from the top of the cell). Place the can, with matt black painted interior, over the sample and obtain the colour value readings L , a and b . Calculate the a/b ratio. As with the red tile, it is important that the sample is not allowed to warm up under the lamp whilst at the specimen port. Readings should be taken as quickly as possible. Standardisation using the red tile should be carried out before reading each set of samples.

DISCUSSION

W. E. L. Spiess asked what other food industry applications of colour measurement there were in addition to those of tomato products. *C. J. B. Brimelow* cited citrus products and coffee—especially different roasts and blends—as important to the consumer. *Spiess* asked if, in the latter case, individual beans or a collection of them were measured. *Brimelow*: Either. For small area colour measurement a Japanese instrument (Minolta) is now available for areas down to 2 mm diameter in standard form. Single beam or large field measurements and integrated computing facilities were available on it, and it could be used for coffee in various forms, including instant powders and granules. *Merken* had measured the colour of coffee roasted to various degrees and ground to different extents and had obtained good correspondence between colour and degree of roast, but the coffee manufacturers had pointed out that it was most important also to taste the coffee; colour alone could be misleading.

Optical Measurements and Visual Assessment of Translucent Foods

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SUMMARY

Colour measurements on translucent foods are affected by instrument geometry, sample presentation and light scatter at sample edges. Increase in the size of potato granules and decrease in illumination aperture diameter both reduced lightness values. The logarithm of the K/S function of reflectance for translucent milk suspensions decreased linearly with increase in aperture size. Problems in relating visual appreciation of appearance to instrumental measurement are illustrated by the results of a study on tomato paste dilutions. Measured lightness increased with solids content at low concentrations but decreased at high concentrations whereas visual assessment using hue descriptors varied linearly with the logarithm of concentration. Visual spacing of colour strength and darkness were directly related to concentration but response to brightness was similar to measured lightness.

INTRODUCTION

The COST 90bis Electrical and Optical Properties subgroup's initial experiments on colour measurement were designed to determine what agreement was achievable among different instruments in interlaboratory trials. As part of that activity, differences in colour between foods and within foods were measured. The results of these studies highlighted the basic problem that the structure of food, its particle size and its light-scattering properties interact with the presentation geometry of the instrument. This is an important source of error unless measurement

procedures are standardised, for example, as in the commercial grading of tomato paste. For foods which are opaque the problem is of relatively small consequence but many foods are, to varying degrees, translucent. The light-scattering properties of such translucent materials not only affect the geometry of reflected light in the instrument (Atkins and Billmeyer, 1966; Hunter, 1975; Hunter and Christie, 1978; Birth, 1978) but can have as much influence on the appearance of food as colour (MacDougall, 1982, 1983). Colour specification alone, therefore, is insufficient to describe the appearance of translucent foods. Some indication of the intensity of light scatter and its relationship to pigment absorption is required as a minimum for appearance specification, although this additional information is still not enough to describe the appearance of strongly-coloured, light-scattering materials in dilute suspension. Small changes in translucence interact with pigment absorption to produce large changes in appearance, which may be so affected by the viewing conditions that what is perceived is vastly different from what might be expected from instrumental measurement. One food product which is a particularly good example of the difficulties involved in relating measurement to appearance is orange juice. Instrumental measurements of brightness give no clear indication of what is observed in a glass of orangeade (Rummens, 1970; Eagerman, 1978), and for dilutions of orange juice the anomalous situation occurs in which the visual appearance of lightness is the opposite of that determined instrumentally (MacDougall, 1983).

Instrument Geometry

Colour-measuring instruments operated in the reflectance mode are usually calibrated with reference materials such as barium sulphate or black, or white or coloured tiles. Apparent incompatibility among instruments may arise from calibration errors—for example, the white might not be corrected to the perfect reflecting diffuser—or from presentation geometry—for example, uncertainty whether to include or exclude the specular component of reflectance. This can lead to discrepancies between measurements obtained from colour-difference meters which exclude the specular and spectrophotometers which allow the choice of either inclusion or exclusion. Sample distortion at the measuring port is another likely source of error if the material is so flexible that it protrudes through the aperture towards the detector.

Most colour-measuring instruments are designed for measuring flat, opaque materials, although the optical geometry of some instruments permits account to be taken of the so-called translucent edge effect. This

occurs where a proportion of the returned light originates from internally-scattered light which emerges beyond the boundary of the illuminated area. Atkins and Billmeyer (1966), in a study of edge loss in translucent materials, showed that light loss through the edges of a white plastic sheet could be as much as 25%. They concluded that the reflectance of thick translucent materials could not be measured with absolute accuracy. The severity of the effect can be reduced if a wide area of surface is illuminated or if the sample is spot illuminated and all the returned light detected. Since there are no generally agreed conditions for measuring transmittance or reflectance of translucent materials (Judd and Wyszecki, 1975), very large differences in measured colour will result if the geometrical conditions are different. Hunter and Christie (1978) demonstrated that increasing the diameter of the viewing port increases the measured lightness of orange juice and tomato paste and affects the apparent hue and chroma of the product, and MacDougall (1983) has shown that both the diameter of the port and the illuminated area interact to alter the measured colour.

Light Scatter

According to the Kubelka-Munk analysis of light transmission through turbid media (Kubelka, 1948; Allen, 1978) reflectivity is related to an absorption coefficient (K) and a scatter coefficient (S) by

$$K/S = (1 - R_\infty)^2 / 2R_\infty$$

where R_∞ is the reflectance of a layer so thick that any increase in thickness does not alter the reflectance. K and S are determined by measuring thin layers of the material over white and black backgrounds which is the procedure commonly used for determining the optical properties of paint, paper and plastics. The technique is fully illustrated by Judd and Wyszecki (1975) and its application in meat and pigmented beverages has been described by MacDougall (1983, 1984a).

Determination of S in some foods may be substituted by the simpler procedure of measuring back-scattered light. This principle is the basis of the FRB fibre optic probe (FOP) used to determine opacity in meat (MacDougall, 1984b; MacDougall and Jones, 1981). Light scatter measured by the FOP is linear with S over the range of lightness in raw meat. The FOP will function similarly in any translucent product which has low absorbance in the near-infra-red; for example, dilutions of evaporated milk over the range of 1–4% solids are used to calibrate the instrument's linearity.

Visual Appearance

Basic to the problem of relating measured colour and light scatter to appearance is the limitation that the direction of the incident illumination in the instrument is different from that used for viewing. Whereas instruments measure reflected light over a limited solid angle, visual appreciation of translucent materials in hemispherical illumination is stimulated by the internally-scattered light which emerges multidirectionally and makes coloured suspensions appear to glow (MacDougall, 1983). That the measurement system can be so vastly different from that for visual observation limits the confidence which can be placed on measured values. The instrument is inadequate, rather than wrong, because it does not measure that synthesis of colour and translucence which human vision perceives as appearance.

TABLE 1
EFFECT OF APERTURE SIZE, ILLUMINATED AREA, PRODUCT PARTICLE SIZE AND CONCENTRATION ON MEASURED LUMINOUS REFLECTANCE (*Y*)

	<i>Luminous reflectance (Y%)</i> <i>Illuminated area diameter/</i> <i>aperture diameter (mm)</i>		
	50/50	20/20	10/20
Potato powder (μm)			
250	78.5	80.6	80.1
500	62.3	60.1	62.4
670	57.6	55.1	58.3
1 000	51.1	46.1	51.5
Evaporated milk (solids %)			
30	73.7	67.9	72.4
10	78.5	71.3	77.0
4	75.0	65.4	72.4
1	55.1	39.4	45.4
Tomato paste (solids %)			
30	5.6	5.5	5.6
20	6.4	6.3	6.4
15	6.7	6.5	6.8
10	6.8	6.4	6.7
Orange juice (relative concentration %)			
100	12.9	11.0	12.2
40	24.8	20.0	22.2
10	18.0	11.9	12.9
3	7.4	4.3	4.7

Collaborative Experiments

In Chapter 23 by Kent on measurement of food colour the results are those obtained for more than one aperture size. The effects of aperture and illumination size for both solid and liquid samples is shown in Table 1. In general, reduction in diameter from 50 to 20 mm had a greater effect on measured luminous reflectance, Y , than changing from diffuse to spot illumination, although spot illumination with 20 mm aperture gave readings that were closer to diffuse illumination with 50 mm aperture. These observations tend to confirm the proposition that spot illumination is superior to diffuse if small apertures have to be used.

For the potato powder, increase in mean particle size reduced lightness because of reduced scatter by the larger particles. Dilution of highly scattering liquids initially increased reflectance which was followed by a decrease as the suspensions became translucent. This decrease is expected from the reduction in scattering power with dilution, but the initial increase is less readily explained. At very high levels of scatter more light is transmitted in the forward direction because of rescattering within the medium. If the particles are so closely packed that dilution increases the effective area of particle surface, then reflectance will increase as back-scatter increases until the maximum area available for scattering light is reached. Only then will decrease in scatter with dilution occur. Naturally, the more concentrated suspensions will also *absorb* more light than the dilute.

EXPERIMENTAL

Two further experiments were carried out. The first examined the relationship between aperture size, light scatter and reflectance, and the second investigated the cause of confusion between optical measurements on tomato paste and its visual appearance.

Evaporated Milk

Evaporated milk (Nestlé, 'Ideal') was diluted with distilled water to give a series of opaque-to-translucent suspensions of from 30 to 2% solids. They were measured on a Hunter D25-M Colour Meter calibrated with a glass plate, the same thickness as the base of the measuring cell, interposed between the aperture and the white and black tiles. The cell was filled to optically infinite thickness (> 5 cm) and the tristimulus values measured for each dilution using 50, 25, 20, 10 and 5 mm diameter apertures with a black cover over the cell to exclude extraneous light.

Tomato Paste

Tomato paste (Nestlé-Londreco) was diluted with distilled water to give a series of concentrations of 30, 15, 10, 7·5, 7, 3·75 and 1·875% total soluble solids. These dilutions were chosen so as to give visual steps approximately equally spaced on the expectation that observer response might be a power function of concentration (MacDougall, 1983). The diluted pastes were measured in the same way as the evaporated milk, on a Hunter D25-A Colour Meter at optically infinite depth using a 5-cm diameter aperture.

The liquids were presented in 4-cm diameter, 50-ml glass beakers filled to a depth of 4 cm to a nine-member panel on three occasions. Each panellist was asked to place the two most different samples at the extremes of a 70-cm long by 7-cm wide strip of white filter paper in a neutral grey viewing booth lit by artificial daylight. To aid the panellist, a narrower strip, 4 cm wide, with a longitudinal black line divided into 10 unnumbered equal segments was laid alongside the wider strip. The remaining samples were then spaced in order between the extremes by the panellist, who assigned numerical values to the differences. Each sample was then viewed separately in random sequence for profiling the appearance attributes of strength (weak to strong), darkness (pale to dark), brightness (dull to bright) and translucence (opaque to transparent) using 10-cm line scales. The colour hue terms purple, red, orange, yellow and brown were assessed from nil to extreme using 10-cm line scales and the greyness was assessed from white to black. The panellists were unaware that the same dilutions, freshly made, were presented at each session.

RESULTS AND DISCUSSION

Evaporated Milk

Increasing the total solids in the evaporated milk suspensions up to about 10% increased the light scatter which increased reflectance (note that increasing reflectance produces decreasing values of K/S) but which thereafter decreased as the suspension became more opaque (Fig. 1). Because of the theoretical additivity of the absorption and scatter coefficients, reflectance for tristimulus value Y has been transposed to the Kubelka-Munk ratio K/S . The values obtained at each aperture were progressively different; the 50-mm aperture produced the smallest K/S values and the 5-mm aperture the largest. The effect of aperture diameter was greater than the effect of concentration. The systematic effect of

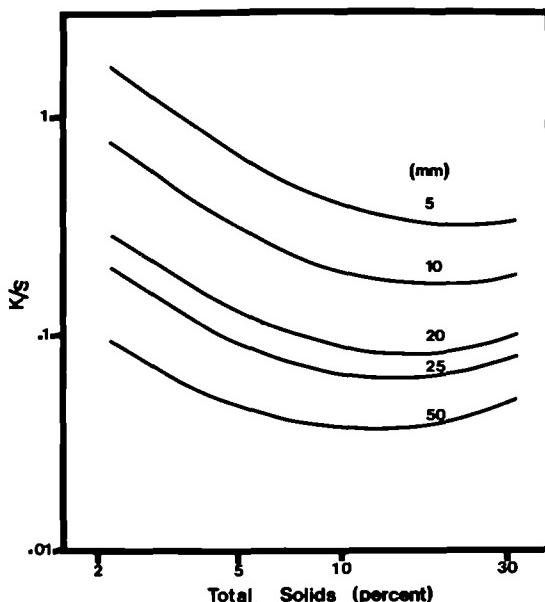


Fig. 1. Effect of aperture size on the relationship between the Kubelka-Munk ratio of absorption to scatter (K/S) for luminous reflectance (Y) and the total solids content of dilutions of evaporated milk.

aperture size is seen in the logarithmic relationship between K/S and concentration which produces near-parallel curves.

These results confirm the observations in Table 1 and emphasise the care required in defining optical geometry when measuring translucent materials. The magnitude of the problem is illustrated in Fig. 2, where the ten-fold decrease in aperture diameter produces a nearly ten-fold decrease in K/S .

Tomato Paste: Panel Assessment

The cumulative mean panel score (CMS) for the differences between samples was linear with the logarithm of concentration for all but the two most dilute suspensions (Fig. 3). The greater difference between the two least concentrated suspensions could be attributed to the dilutest tending to precipitate because of the low viscosity. This result for the visual spacing of tomato paste is virtually identical to that for orange juice (MacDougall, 1983). The orange juice trial indicated that the straight-line spacing was related to the straight-line change in measured hue and chroma with the

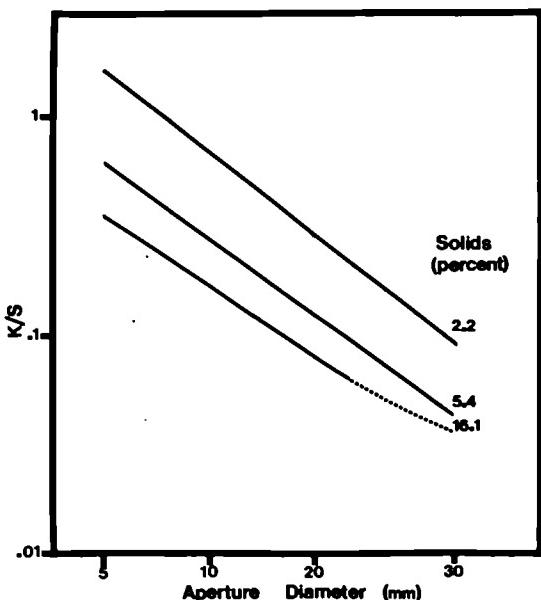


Fig. 2. Approximately straight-line relationship between the logarithm of K/S for Y and the logarithm of aperture area for dilutions of evaporated milk.

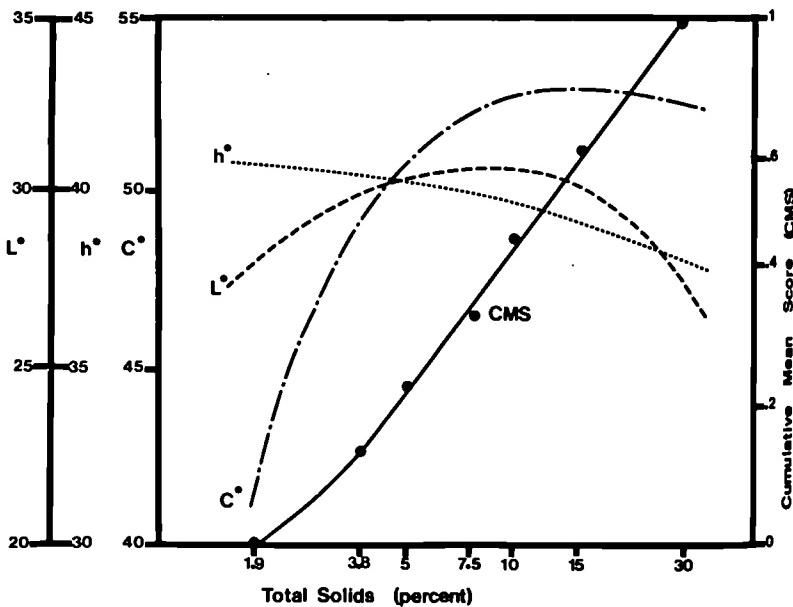


Fig. 3. Relationship of CIELAB lightness (L^*), hue angle (h^*), chroma (C^*) and of the cumulative mean panel score (CMS) between adjacent samples to the logarithm of the total soluble solids content of a series of suspensions of tomato paste.

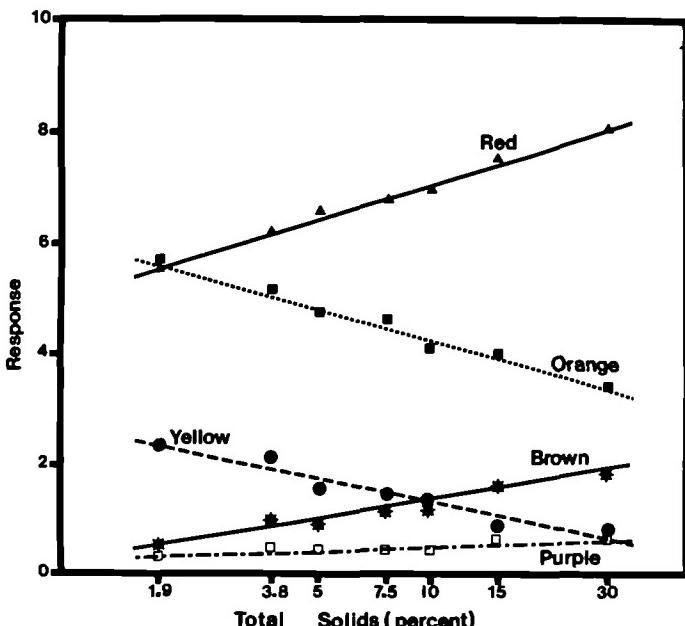


Fig. 4. Relationship between panel mean response to the colour profile descriptors and the logarithm of the total soluble solids content of a series of suspensions of tomato paste.

logarithm of concentration. However, assessment of other appearance attributes was not attempted in that trial. The panellists' estimate of spacing of colour terms for tomato paste confirms that systematic relationships exist between visual spacing and colour terminology.

Panellists' use of hue descriptors was linear with the logarithm of concentration (Fig. 4), the greatest response and greatest change occurring for red and orange. As red increased with solids content orange decreased, indicating a distinctly recognisable change in hue. The yellow followed the orange but with smaller response values, and brown similarly followed red. Increase in purple also followed increase in red but its response was less than 10% of that of red. The panel found it impossible to assign values to the hueless colour attribute 'grey' for tomato paste.

Response to the non-colour appearance terms was not linear with the logarithm of concentration (Fig. 5). Deviation from linearity tended to be associated with the more concentrated suspensions. There was unambiguous agreement that the most concentrated suspension was the darkest,

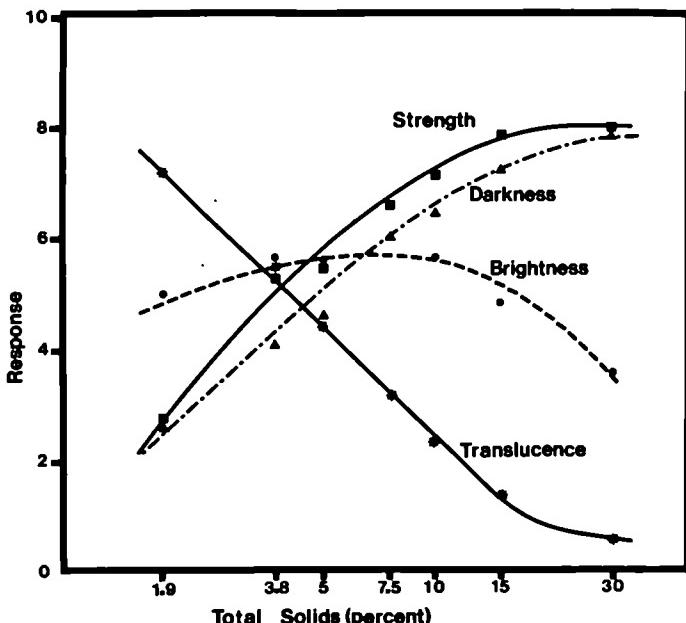


Fig. 5. Relationship between panel mean response to the appearance profile descriptors and the logarithm of the total soluble solids content of a series of suspensions of tomato paste.

strongest and least translucent (most opaque). Brightness increased with dilution from the most opaque to about 10% solids and then decreased slightly. This phenomenon is similar to that observed with orange juice, where visual brightness is affected by the interaction of light scatter in the suspension and the directionality of the viewing illumination, causing the product to glow.

Comparison of the panel's spacing and term usage with the psychometric interpretation of the colour (Figs. 3 and 4) would indicate that change in hue angle and chroma could be interpreted as responsible for the appreciation of strength and darkness of the product. However, the incongruity that measured lightness does not agree with the observed response negates any confidence or reliance on colour values or their psychometric interpretation as true or sufficient indicators of appearance. What is clearly evident is the relationship of the cumulative mean score of visual differences to the visual assessment of translucence and the instrumental measurement of light scatter. Of considerable importance in

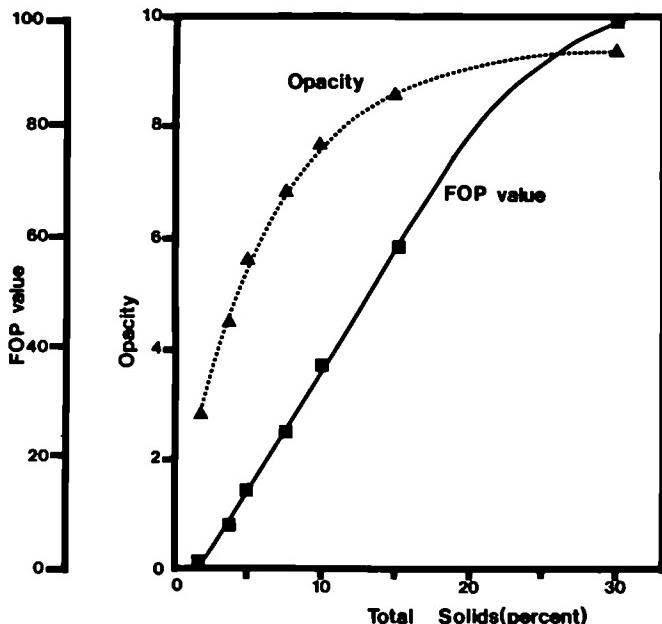


Fig. 6. Comparison of straight-line dependence of light scatter (FOP value) to the total solids of a series of suspensions of tomato paste with the visual assessment of opacity (10-translucence).

the understanding of cause-and-effect relationships between optical properties and appearance are the relationships in which light scatter is a linear function of the concentration of scattering elements (Fig. 6) whereas visual appreciation is a logarithmic function of concentration.

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The Colour of Potato Products

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INTRODUCTION

The colour of dehydrated potato products which varies between pale and deep yellow is closely related to the colour of the raw potato tubers. Nevertheless, processing conditions may influence the colour of products considerably, producing enzymic discoloration or after-cooking blackening. Carotenoid pigments (xanthophylls) e.g. violaxanthin, lutein, lutein- β, β -epoxide, along with several mono- and diesters are responsible for the colour of the raw potato and the processed products (Iwanzik *et al.*, 1983; Tevini and Bergthaller, 1985; Tevini *et al.*, 1984). Fried potato products (crisps and French fries) exhibit additionally a browning due to Maillard reactions. Work on colour measurement of dehydrated potato products had been very limited but recently several studies on the measurement of dehydrated diced potato have been published (Bergthaller *et al.*, 1978; Bergthaller and Kempf, 1980; Schaller *et al.*, 1980; Bergthaller *et al.*, 1983). For the measurement of colour of potato crisps numerous attempts and procedures have been reported, however (Grünewald, 1974; Francis and Clydesdale, 1975).

METHODS

For instrumental measurement of the colour of dehydrated potato products a tristimulus colorimeter, Momcolor model D has been used. Specific details on the colorimeter, illuminant source, standard for calibration, sample preparation and conditions of measurement are given by Bergthaller *et al.* (1978). Measured tristimulus values are transformed

into colour coordinates in the usual way. With crisps an abridged spectrophotometer Agtron model M500A is used to measure degree of browning. For calibration, plastic discs (M-00 and M-68) are used to set zero (black) and a hundred scale points (pale grey) as internal standards. The illuminated area is about 52 cm². Reflection measurements at four selected wavelengths (436, 546, 585 and 640 nm) are combined to give total reflection values. Crisp samples have been measured after 50% compression to a final sample layer of 40 mm.

RESULTS

The colour locus of dehydrated diced potatoes shows a very narrow chroma range (dominant wavelength: 575–8 nm). They differ mostly in purity and lightness. Since this material varies in particle size and shape the effect of size has been studied. Particle size is of significant influence on lightness and chromaticity. This effect does not encourage size reduction in sample preparation since reproducibility is not improved thereby.

Using a transformation from CIE to Hunter Lab scales a good differentiation between samples of dehydrated diced potatoes is achieved. Lightness (*L* value) varies from 37 to 58 and the yellow component (*b* value) from 13·7 to 23·2. The range of *a* values (red-green component) is –1·8–+0·8. Nevertheless even small *a* values seem to influence sensory evaluation (Schaller *et al.*, 1980).

Colour measurement on dehydrated potato flakes/granules is said to be

TABLE 1
RESULTS OF COLOUR MEASUREMENTS ON COMMERCIAL POTATO PRODUCTS FOR PURÉE PRODUCTION

Product type	Number of samples	CIE colour coordinates		
		<i>a</i> *	<i>b</i> *	<i>L</i> *
Flakes	6	Mean ^a	–5·63	29·63
		sd ^b	0·596	0·377
		Min.	–5·86	28·61
		Max.	–5·26	30·46
Granules	1		–3·47	28·26
				87·0

^a Weighted mean.

^b Weighted standard deviation.

TABLE 2
RESULTS OF COLOUR MEASUREMENTS ON COMMERCIAL POTATO DUMPLING FLOURS

Product type	Number of samples	CIE Lab colour coordinates			
		a	b	L	
Raw dumplings	4	Mean ^a	-2.99	15.81	88.8
		sd ^b	0.665	0.369	0.11
		Min.	-3.15	15.30	88.7
		Max.	-2.86	16.40	89.0
Raw dumplings (exceeding shelf life by 9 years)	1		+0.80	20.08	78.7
Half and half dumplings	7	Mean ^a	-2.81	14.56	89.9
		sd ^b	0.386	0.258	0.06
		Min.	-2.99	11.93	87.8
		Max.	-2.60	16.98	91.4
Cooked dumplings	4	Mean ^a	-3.76	19.39	89.4
		sd ^b	0.389	0.212	0.06
		Min.	-3.92	18.31	88.6
		Max.	-3.67	20.50	89.7

^aWeighted mean.

^bWeighted standard deviations.

not complicated because this colour is stable and homogeneous (Grünwald, 1974). However, Francis and Clydesdale (1975) recommend careful control of particle size, but measurements carried out recently do not confirm a definite influence of particle size of dehydrated potato flakes except for the very fine fraction (<250 µm) (Berghaller, 1986). The sample layer thickness does not influence CIE Lab colour coordinates significantly within the range 10–40 mm, so a sample layer of approx. 20 mm has been used in measurements of commercial products (Table 1).

Methods of colour measurement for commercial potato dumpling flours have proved to be suitable for dehydrated potato flakes and other product types (Table 2).

The colour of potato crisps has been graded by sensory evaluation for a long time, but following trends, is turning to instrumental measurements. In order to meet the differing aims of research and industry the relationship between total reflection values and colour grades has been established on the basis of about 1000 samples. Now, a table for conversion of total reflection values to sensory colour grades has been assembled (Putz, 1981).

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Instrumental Measurement of White Sugar Colour

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The determination of the quality of a white sugar is specified in EEC regulations; apparent whiteness, is one of the characteristics.

The visual whiteness evaluation is made by comparing the sample with seven reference samples of decreasing whiteness, known as the Braunschweig scale, and given a rating between 0 and 6.

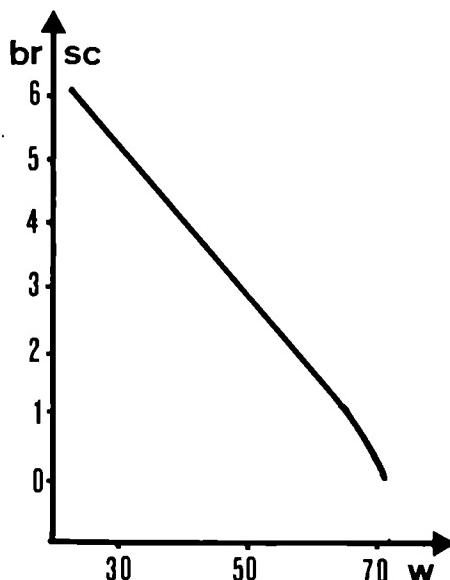


Fig. 1. Relationship between instrumental whiteness (w) and visual whiteness on the Braunschweig scale ($br sc$).

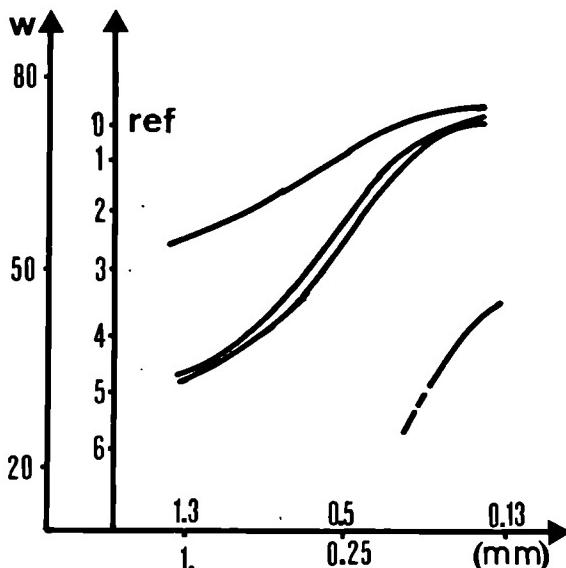


Fig. 2. Effect of particle size (mm) on whiteness of sugar as measured by instrumental (*w*) and visual (*ref*) methods.

To avoid disputes an instrumental colour measurement is proposed. The variety of whiteness formulae available led to the involvement of CIE and to the proposition

$$w \text{ (whiteness)} = y + 800(x_n - x) + 1700(y_n - y)$$

where *x* and *y* are chromatic coordinates. The accord of the instrumental measurement (*w*) with visual evaluation on the Braunschweig scale is satisfactory (see Fig. 1).

The influence of the crystal size is quite important. It is possible to 'upgrade' the whiteness of a sugar by grinding to a smaller particle size. The accord of the instrumental method with the visual is still satisfactory, as Fig. 2 shows.

The Colour of some Spanish Wines

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I. METHOD OF COLOUR MEASUREMENT

1. Introduction

Almost all the publications on wine colour studies cited in *Food Science and Technology Abstracts* since 1980 use simplified methods, mainly the Sudrau Index (Sudrau, 1958) and the OIV official method (Stella, 1968), for wine colour characterisation. Only Riva's (1979) method uses the complete spectrum in the form of trichromatic coefficients, with the aid of a computer. None uses uniform coordinate systems or determines colour differences. Two reasons for such a situation are:

- (a) The need for powerful computer-based equipment to determine colour coordinates over the complete spectrum as a routine.
- (b) The convenience offered by simplified methods of colour measurement (SMCM) for industrial work.

Nevertheless, SMCM are not very suitable for all the varieties and types of wines (Riva, 1979).

It seems, then, potentially profitable to make use of computer-aided spectrophotometers to typify the colour of wines by complete spectrum measurements and also to use them to test and correct the proposed simplified methods.

2. Equipment

A 'diode-array' spectrophotometer (Hewlett Packard HP8451) with a computer (HP85) was used for spectra determination. Each spectrum was formed from the transmittance values at each 5 nm interval between 360 and 775 nm and is stored in files designated 'COSTFILE'.

Normalised colour coordinates (CIE, CIELAB, HUNTER and Psychometrics) may be obtained either from complete 'COSTFILE' spectra or by simplified methods. Calculations are based on the 10° observer and illuminant D65. Results obtained are stored in a file designated 'DATACOST'. Afterwards they are treated by BMDP statistical software (Brown *et al.*, 1981).

II. CHROMATIC BEHAVIOUR AND SIMPLIFIED METHODS FOR COLOUR MEASUREMENT OF RED WINES

Table 1 shows the wine samples used in the test. All were new wines of 1985 vintage. Each sample was centrifuged and placed in a glass sample cell 1 mm thick, for measurement. Transmittances obtained in this way were transformed into the equivalent values for a sample cell 10 mm thick, by using eqn. (1).

$$T(10 \text{ mm thick}) = [T(1 \text{ mm thick})]^{10} \quad (1)$$

The values of the trichromatic coefficients for red wines correlate very closely with eqn. (2).

$$y = 0.779 - 0.695x \quad (**) \quad (2)$$

The experimental points lie in a very narrow space, in the range: $0.673 < x < 0.718$ and $0.281 < y < 0.300$, with a dominant wavelength of 624–40 nm and colour purity between 94 and 99%.

As the CIE coordinates cannot be used to calculate colour differences, CIE Lab coordinates were calculated and correlated. Equations (3)–(5) resulted for all samples. In all cases the significance level was 99%.

TABLE 1
DISTRIBUTION OF RED WINE SAMPLES

<i>Variety</i>	<i>Number of samples</i>	<i>Origin</i>
Garnacha	117	Rioja
Garnacha	11	Requena
Tempranillo	15	Rioja
Tempranillo	4	Requena
Bobal	35	Requena
Total	183	

Nevertheless, an $L^*(a^*)$ relationship was found to be the best for characterising the colour of red wines. This is logical, because a^* gives a measure of the red content of each sample.

$$L^* = 0.604a^* - 14.474 \quad (**)$$
 (3)

$$L^* = 0.381b^* - 3.085 \quad (**)$$
 (4)

$$a^* = 0.621b^* - 19.174 \quad (**)$$
 (5)

It is concluded that the use of CIE Lab coordinates (especially $L^*(a^*)$) is preferable for specifying the colour, and colour difference, of red wines.

The tristimulus coordinates XY , calculated from the complete spectrum, have been compared with those calculated by the OIV method (Stella, 1968) and correlated by eqns. (6) and (7). In all cases, the value of Z was near zero. Nevertheless, a correlation for $Z(Z_0)$ was achieved.

$$X = 0.167X_0 \quad (**)$$
 (6)

$$Y = 0.136Y_0 \quad (**)$$
 (7)

$$Z = 0.957Z_0 \quad (**)$$
 (8)

It is clear that the OIV simplified method is not able to determine with sufficient accuracy the colour coordinates of Spanish red wines. With the OIV method equations and eqns. (6)–(8), three new equations have been derived, as follows:

$$X_c = 0.070T_{625} + 0.058T_{550} + 0.035T_{445} \quad (9)$$

$$Y_c = 0.027T_{625} + 0.085T_{550} + 0.023T_{445} \quad (10)$$

$$Z_c = 0.234T_{495} + 0.900T_{445} \quad (11)$$

III. CHROMATIC BEHAVIOUR AND SIMPLIFIED METHODS FOR MEASUREMENT OF WHITE WINE COLOUR

Table 2 shows the distribution of white wine samples tested. Experimental conditions were similar to those for the red wine case, but a 10 mm glass sample cell was used in the colour measurements.

As with red wines, xy values have been correlated with the correlating eqn. (12). A $Y(x, y)$ relationship was also obtained (eqn. (13)).

$$y = 1.139x - 0.026 \quad (**)$$
 (12)

$$Y = 273.0 - 884.5x + 319.3y \quad (**)$$
 (13)

TABLE 2
DISTRIBUTION OF WHITE WINE SAMPLES

Variety	Number of samples		Origin
	1984	1985	
Palomino fino	19	23	Rueda
Verdejo blanco	4	11	Rueda
Viura	2	2	Rueda
Varietal mixtures	3	—	Rueda
Total	28	36	

The colour behaviour is typified by a straight line, in the range of dominant wavelength of 337–55 nm and 8–22% of colour purity. No influence of variety or vintage on colour behaviour was observed.

Again, as with red wines, the CIE Lab coordinates provide an accurate basis on which to typify colour and to determine colour differences; but here, the best relationship seems to be $L^*(b^*)$, as might be expected, because the b^* coordinate gives a measure of the yellow content. The equations obtained correlating the CIE Lab coordinates were:

$$L^* = 1.006a^* + 98.343 \quad (0) \quad (14)$$

$$L^* = -0.349b^* + 100.662 \quad (***) \quad (15)$$

$$a^* = 0.848b^* + 0.016 \quad (**) \quad (16)$$

The tristimulus coordinates XYZ , calculated from the complete spectra, have been compared with those calculated by the OIV method and are correlated by eqns. (17)–(19).

$$X = 1.001X_0 - 3.836 \quad (**) \quad (17)$$

$$Y = 1.113Y_0 - 11.574 \quad (**) \quad (18)$$

$$Z = 0.997Z_0 - 11.002 \quad (**) \quad (19)$$

The following equations have been obtained from equations of the OIV method and eqns. (17)–(19):

$$X_c = 0.42T_{625} + 0.35T_{550} + 0.21T_{445} - 3.83 \quad (20)$$

$$Y_c = 0.22T_{625} + 0.70T_{550} + 0.19T_{495} - 11.57 \quad (21)$$

$$Z_c = 0.24T_{495} + 0.94T_{445} - 11.0 \quad (22)$$

Equations (20), (21) and (22) represent a simplified method of colour measurements for white wines.

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Part 4

MECHANICAL PROPERTIES

Mechanical Properties of Solid Foods— Deformation, Fracture and Stress Relaxation

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SUMMARY

The structural and compositional complexities of solid foods make it advantageous, perhaps essential, to evaluate their mechanical properties by more than one experimental technique. By comparing results from different testing modes, problems in methodology may be discovered and lead to a greater understanding of the mechanical behaviour and of the structure/composition/processing interrelationships. Foods that undergo relatively large deformations before fracture present particular difficulties because of time-dependent effects during measurement. Despite recent progress, such materials, with behaviour governed by a broad spectrum of relaxation times, need better quantitative methods of describing time effects in stress growth during deformation and stress relaxation after deformation. The frictional properties of foods need fuller investigation, to improve both understanding of texture profile analysis tests and their relationship to sensory perception of foods.

INTRODUCTION

Determination and evaluation of the physical properties of solid foods present many difficulties to the scientist, as described so succinctly by Prins and Bloksma (1983). Solid foods are often heterogeneous and anisotropic. Sample history can be crucial, with results dependent not only on such factors as rate and extent of deformation but also on the sample history, which includes processing and storage effects prior to measurement. Consider the determination of the response of a solid food to torsion. It is

necessary at some point to place the sample on an instrument between two parallel discs. In this manipulation, forces are exerted on the sample and it can take a considerable time for these forces to relax so that the stable baseline necessary for the actual experiment may be obtained. Not only is this time-consuming but, because of the high water activity of many food systems (for example gels), the sample may start to dry out. Crust formation can then lead to erratic results. Humidity control is then necessary to prevent sample drying. Depending on the actual equipment being used, humidity control is not always easy.

Another problem can be that of attaching the sample to an instrument. For example, in experiments by Navickis and Bagley (1983) on a solid material consisting of a close-packed dispersion of swollen starch particles, the sample was placed between metal platens and large deformations applied in simple shear. Initial shear stress/shear strain results were erroneous because the sample slipped on the plates. The problem was detected only because the results, superficially acceptable, were internally inconsistent. Resolution of the difficulty was achieved by bonding the sample to the instrument platens with a cyanoacrylate adhesive, which has since been shown to be an ideal material for bonding a wide range of food materials, including meats and water-based gels and dispersions, to metals.

On a more fundamental level, mechanical testing of solid foods is so broad in scope that it is essential to assess carefully the objectives of the work being undertaken. The scope may be relatively narrow, concerned, for example, with quality or process control, or it may be broader and deal with such problems as component interactions in complex mixtures. Notwithstanding limited immediate objectives, the range of application, and the implications, of technical results may develop beyond those limits. Opportunities present themselves and new avenues of approach are opened. The best way of ensuring the value and meaning of the results obtained in measurements on foods, therefore, is to discuss the 'deformation, fracture and flow of food materials in terms of fundamental units of physics' (Hamann, 1983). Sound engineering input is also needed, and this point was emphasised by Jowitt (1979) and Szczesniak (1977). Progress in polymer research and material science can provide guidance for food scientists in methodology and data analysis. Even though foods suffer from complexities which are usually not present in polymer systems (biological activity, for example), many useful techniques and concepts may be transferred from polymers and their blends, including composites, to food systems. Jowitt (1979) has discussed some aspects of this with reference to fracture processes and the behaviour of laminated food.

The objectives of this chapter are: to show the advantages of using various testing modes in evaluating the physical properties of foods; to examine strain and time effects; and to suggest some areas worthy of continued research effort.

THEORETICAL BACKGROUND

Stress-Strain Relations

There is extensive literature on the mechanics of polymers which is relevant to the consideration of the mechanical properties of foods. Useful references include Williams (1973) on stress analysis of polymers, Treloar (1975) on physics of rubber elasticity, and Kinloch and Young (1983) on fracture behaviour of polymers. Familiarity with the terminology and use of tensors is necessary for reading much of the rheological literature and a useful textbook in this subject area is provided by Darby (1976).

Rheologically, the question as to whether a particular food is a solid or a liquid should be considered in terms of the non-dimensional Deborah number, D , defined by Reiner (1964) as the ratio of the relaxation time of the sample divided by the time of observation. In Reiner's words: 'The difference between solids and fluids is then defined by the magnitude of D . If time of observation is very long or, conversely, if the time of relaxation of the material under observation is very small, you see the material flowing. On the other hand, if the time of relaxation of the material is larger than your time of observation, the material, for all practical purposes, is a solid.' Time is, in general, a crucial variable when investigating the mechanical properties of foods. It is necessary to determine not just a stress-strain curve but the stress-strain-time relationships describing the behaviour of the material. For complex foods there is an artificial distinction between solid and liquid states, which depends not only on the material but also on the experimental time scale relevant to the specific use of the food or the specific process to which the food is subjected.

There is no ambiguity in the definition of stress, the force per unit area. There are, however, various ways of defining strain. The classical definition of infinitesimal strain will normally be applicable only for small deformations. For large deformations Peleg (1984) has compared strain definitions such as Hencky's, Almansi's, Green's and Swainger's with the terms of Mooney's equation for compressive deformation. Mooney's two-term relationship, discussed by Peleg, is of particular interest as a special case of the more general approach to the large deformation behaviour of

isotropic materials as discussed by Rivlin in his review (1956) and applied to rubber-like materials by Treloar (1975). The value of the approach is that a stored-energy function, W (from which the stress-strain response of the material can be derived), is written in terms of three strain invariants, I_1 , I_2 and I_3 . These invariants are defined as follows: A cube of side length 1 cm is deformed to dimensions λ_1 , λ_2 , λ_3 . The strain invariants are then given as

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \quad (1)$$

$$I_2 = \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_3^2 \lambda_1^2 \quad (2)$$

$$I_3 = \lambda_1^2 \lambda_2^2 \lambda_3^2 \quad (3)$$

I_3 represents the volume of the cube after deformation and, if the material is incompressible, the value of I_3 during deformation is constant at unity. The stored energy function will then be given as

$$W = W(I_1, I_2) \quad (4)$$

If a form is assumed for the stored energy function, it becomes possible to calculate the expected stress-strain relationship for given deformation modes, such as simple shear, torsion, compression, extension, etc. A two-constant Mooney material is described by the strain energy function

$$W = C_1(I_1 - 3) + C_2(I_2 - 3) \quad (5)$$

For three common deformation modes—extension/compression, simple shear and torsion—the stress-strain relationships for a Mooney material assume the forms:

Extension/compression

$$f = 2(\lambda - 1/\lambda^2)(C_1 + C_2/\lambda) \quad (6)$$

where f is the force per unit area measured in the unstrained state.

Simple shear

$$\tau = 2(C_1 + C_2)\gamma \quad (7)$$

where τ is the shear stress, γ is the shear strain, and $2(C_1 + C_2)$ is the shear modulus, G . The material thus obeys Hooke's law in shear.

Torsion

$$M = \pi \psi a^4(C_1 + C_2) \quad (8)$$

$$N = -(\pi/2)\psi^2 a^4(C_1 + 2C_2) \quad (9)$$

where M is the torque, N is the normal stress, ψ is the torsional strain ($\psi = \theta/h$, θ being the angle of twist and h the sample height), and a is the sample radius.

The assumption that the stored energy function can be described by eqn. (5) is restrictive and, as Treloar (1975, Chapter 10) comments, 'great care must be exercised in drawing general conclusions from the apparent agreement with the Mooney theory obtained experimentally'. He goes on to note that any particular type of strain provides too narrow a basis for determining the true form of W . Nevertheless, the relationships given by eqns. (6)–(9), based on the Mooney theory, are excellent starting points for considering experimental data from different test modes. Deviation of experimental results from expected values necessitates a more general treatment of the data involving derivatives $(\partial W/\partial I_1)$ and $(\partial W/\partial I_2)$ rather than C_1 and C_2 . It is only by considering all types of strain over a wide range that a true assessment of material properties and not one limited by a particular test can be expected. Hamann has also commented on the need for results which are not dependent on a specific test geometry (Hamann, 1983) and compared the results of structural failure in simple shear, torsion and uniaxial compression using Mohr's circle procedure.

Time, Yield and Fracture Effects

Solid foods will often show complex time effects, as illustrated by Olkku and Sherman (1979) (their Figs. 12 and 13). These show stress-strain response curves for liquorice. It is sometimes convenient and useful when considering a large quantity of rate-, time- and deformation-dependent data to use rheological models to describe the material's response. As in the polymer field, various combinations of Maxwell and Voigt elements, as well as other combinations of springs and dashpots, can be used to develop equations to reduce data quantitatively. Peleg and colleagues have been major proponents of this approach, but in treating mechanical properties of solid foods they have found it necessary to add contact and fracture elements to the more common linear viscous and elastic elements to explain the various memory phenomena observed (Peleg, 1977; Pollak and Peleg, 1980). The paper by Calzada and Peleg (1978) demonstrates clearly the type of stress strain/strain rate responses observed in such diverse materials as bread, turnip, bologna sausage and squash. Peleg and co-workers have also shown the advantages of computer-aided characterisation and classification of solid foods (Miller *et al.*, 1986; Peleg and Normand, 1982; Purkayastha *et al.*, 1985), while keeping in mind the need to relate the results to sensory perception (Peleg, 1980a, 1978).

Time effects, both during and after deformation (as in stress relaxation studies), are important in many food systems. As Feltham (1955) expounded, there is 'remarkable qualitative similarity in the response of solids of widely different structures', including polymeric solids, ceramics and other materials whose log-normal distribution of relaxation times leads to linear stress relaxation plots on probability paper. The method has been used in food materials by, for example, Shelef and Bousso (1964). Peleg (1980b) and Peleg and Normand (1983) compare other methods for obtaining linear stress relaxation and creep curves, but there are fundamental issues which need greater attention. The problem is that stress relaxation curves depend on the time it takes to deform the sample. Thus, if a deformation is completed in t_1 s, then the 'rule-of-ten' requires that only relaxation data at times greater than $10t_1$ be used in analysing the results. The problem is not easily dealt with but the paper by Meissner (1978) shows one method of treating stress relaxation in polymeric liquids and solids by assuming that the materials are linearly viscoelastic and the strain history is one of constant strain rate in the period $0 < t < t_1$ followed by a constant strain for $t > t_1$. Other approaches which have not been applied to solid foods but which show promise include the use of an integral constitutive equation as, for example, in the work of Zapas and Phillips (1971).

Complementary Testing Modes—Some Experimental Results

Gels are of particular interest because their mechanical behaviour should be described by rubber-like elasticity theory, specifically by the Mooney two-constant equation. Attention should be given to the review of gel behaviour by Mitchell (1976) and to recent original contributions (Sherman, 1982; Ring and Stainsby, 1982; Richardson *et al.*, 1981; Dahme, 1985; McEvoy *et al.*, 1984). These works indicate the long-term and continuing activity which exists in the examination of the physical properties of gels and gel-like foods. A surprising result was obtained at the author's laboratory when carrying out experiments on the behaviour of gelatin gels in simple shear, torsion and compression. It was found that the material followed the Mooney equation in two of the modes, simple shear and torsion, but showed very large deviations from the expected behaviour in compression (Bagley *et al.*, 1985a). The problem was traced to frictional losses at the sample/platen interface during compression. Elimination of these effects by either lubricating or bonding the surfaces of the samples in contact with the compression plates yielded results in complete agreement with those from simple shear and torsion experiments (Bagley *et al.*, 1985b).

The magnitude of frictional effects in uniaxial compression of wheat

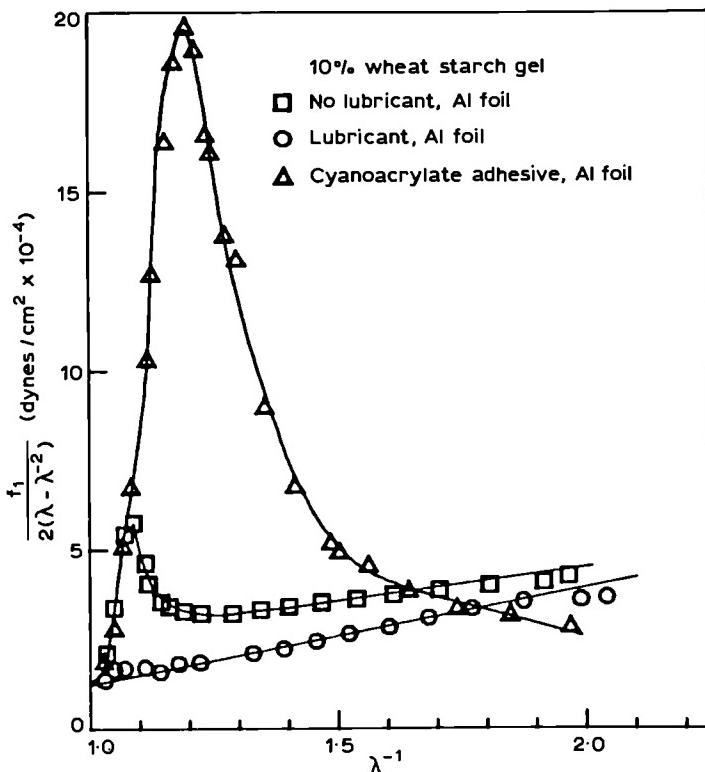


Fig. 1. Uniaxial compression of cylinders of a 10% wheat starch gel using aluminium foil as interface between platens and gel. Upper curve is the response when the gel is bonded to the aluminium foil; middle curve, neither bonded nor lubricated; lower curve, lubricated between gel and aluminium foil. Nominal radii and heights were 3.85 and 1.2 cm (from Bagley *et al.*, 1985a).

starch gels is illustrated in Fig. 1. The results were plotted in the form given by eqn. (6); that is, as $f/2(\lambda - \lambda^{-2})$ versus λ^{-1} . The three curves in Fig. 1 correspond to the following experimental conditions: (a) gel bonded to the platens; (b) gel neither bonded nor lubricated; (c) gel/platen interface lubricated. The result obtained under lubricated conditions gave values of $(C_1 + C_2)$ in agreement with those obtained from simple shear and torsion experiments. Under conditions in which the sample was bonded to the platens the curve rose very steeply, and fracture occurred at the peak of the curve. This peak value of $f/2(\lambda - \lambda^{-2})$ in bonded compression was almost 20 times the value obtained under lubricated conditions. Under 'normal'

conditions, that is neither bonded nor lubricated (NBNL), the value of $f/2(\lambda - \lambda^{-2})$ rose initially along the same curve as for the bonded experiment. During this part of the compression the sample sticks to the platens and thus behaves as if it were bonded, with values of $f/2(\lambda - \lambda^{-2})$ as much as six times greater than those obtained under lubricated conditions. At about $\lambda^{-1} = 1.1$ the sample begins to slip along the platens and $f/2(\lambda - \lambda^{-2})$ begins to drop, goes through a minimum and then rises to form an asymptote to the curve obtained under lubricated conditions. The non-bonded-non-lubricated (NBNL) curve always lies significantly above that obtained in lubricated compression.

This result should not have been unexpected. Forster, in 1955, had recognised the importance of frictional effects in compression work on rubbers (Forster, 1955), although he did not compare the lubricated and unlubricated cases. Culoli and Sherman (1976) and Vernon Carter and Sherman (1978) made it abundantly clear in their work on cheese that frictional effects can be crucial in compression studies. The reason for the large quantitative effects observed lies in the change in sample shape which occurs during compression when the sample sticks or is bonded to the compressing platens. When sticking occurs, instead of a cylindrical sample deforming under compression to a cylindrical sample of smaller height the sample changes shape, becoming barrel-shaped. This change in shape is demonstrated nicely in photographs of Gouda cheese during compression (Culoli and Sherman, 1976). The barrel shapes were also observed during compression of Leicester cheese (Vernon Carter and Sherman, 1978). Culoli and Sherman show the quantitative changes they observed in the force/compression curves for Gouda cheese when the compression was carried out under lubricated conditions and when the sample/platen interface was a high friction surface (emery paper). The effects were much less than reported by Bagley *et al.* (1985a), and this may be due to slipping and tearing of the Culoli and Sherman sample at the emery surface. Rate effects are undoubtedly significant here, and in the work on Gouda cheese deformation rates from 2.5 to 50 cm min⁻¹ were employed. These were considerably higher than the deformation rates employed in the experiments described in Fig. 1.

The results in Fig. 1 illustrate the advantages of comparing the response of food materials to different testing modes. Not only can anomalies occurring in one mode be uncovered but it may be possible to quantify the magnitude of the unexpected effects. In the testing of gels as described above, their behaviour in compression could be predicted from the simple shear and torsion experiments. The expected curve was the one obtained

only under lubricated conditions. The results of the first experiment, which was carried out with the sample neither bonded nor lubricated, disagreed with this expectation and led to the investigation into the reasons for the discrepancies. Direct comparison, therefore, between bonded, lubricated and NBNL compression gives a clear indication of when slip/stick effects are occurring in NBNL experiments, and the quantitative evaluation of the effect of friction becomes possible.

Quantitative Treatment of Effect of Change of Shape

It was surprising that the change in sample shape from a cylinder to a barrel shape caused such large effects. It has been possible to derive an expression to take account of this change of shape (Christianson *et al.*, 1985). With this analysis direct comparison of results of bonded and lubricated compression becomes possible (see also Casiraghi *et al.*, 1985). The magnitude of the correction is related to the fact that in lubricated compression the sample is in biaxial extension while in bonded compression, or when friction predominates or when the sample sticks to the platens, the material forms a parabolic bulge; the material in this bulge is under shear, and the consequences both for the stress-strain curves and for the fracture of the material can be quantified (Christianson *et al.*, 1985).

Figure 2 shows the changes in sample shape occurring under lubricated and bonded conditions. From the analysis (not confined to small deformations), using the procedure developed by Gent and Lindley (1959), the *corrected* stress, σ_{BC} , in the bonded condition is

$$\sigma_{BC} = \sigma_B / \left[1 + \left(\frac{R_0^2}{2h^2} \right) \right] \quad (10)$$

where

$$\sigma_B = \text{force}/\pi R_0^2 \quad (11)$$

At a given strain ($\Delta h/h$), σ_{BC} versus $(\Delta h/h)$ should agree with the stress-strain behaviour in lubricated compression, with the stress in the lubricated case calculated as

$$\sigma_L = \text{force}/\pi R^2 \quad (12)$$

Figure 3 demonstrates the efficacy of the analysis. Note first that the same stress-strain curve is obtained in lubricated compression regardless of initial sample height (dotted line, Fig. 3, initial heights, $h_0 = 2.0-4.0$ cm). However, fracture occurs at smaller stresses with greater initial heights h_0 . For bonded samples the stress σ_B depends very significantly on initial sample height (Fig. 3, 'bonded' curves). Note the very large values of stress

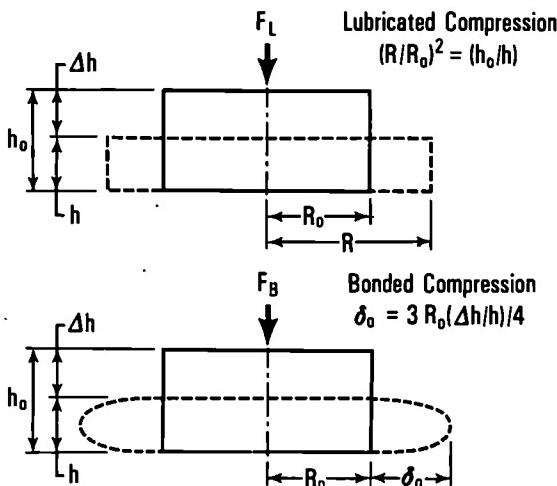


Fig. 2. Deformation of cylindrical samples in lubricated and bonded compression: solid line, original elevation; broken line, deformed elevation (Christianson *et al.*, 1985).

compared to those for the lubricated cases. Correction of σ_B , however, by the term $(1 + R_0^2/2h^2)$ gives σ_{BC} versus strain curves in good agreement with the lubricated compression experiments up to the point of fracture. In bonded compression, however, fracture occurs at lower stresses when corrected for shape change than in lubricated compression and, moreover, fracture stress *increases* with increasing initial sample heights from 1·2 to 4·0 cm for the bonded samples.

Forging Theory Applied to Gels

There appear to be many opportunities to apply concepts from mechanics of materials to problems in the testing of foods. A most interesting example is the application of forging theory to the determination of the modulus of alginate gels (Mohamed, 1983). Mohamed, referring also to the work of Olkku and Sherman (1979), notes that under compression a viscoelastic substance assumed a barrel shape and discusses in detail the stresses existing in the gel and develops equations for use with compression data. In the forging theory treatment the coefficient of friction is important and Mohamed comments that 'there is at present no generally accepted method of measuring the value of the coefficient of friction for given surfaces and lubricants', and has reported that as the frictional contribution to the applied force does not exceed 10–20% approximate values of the

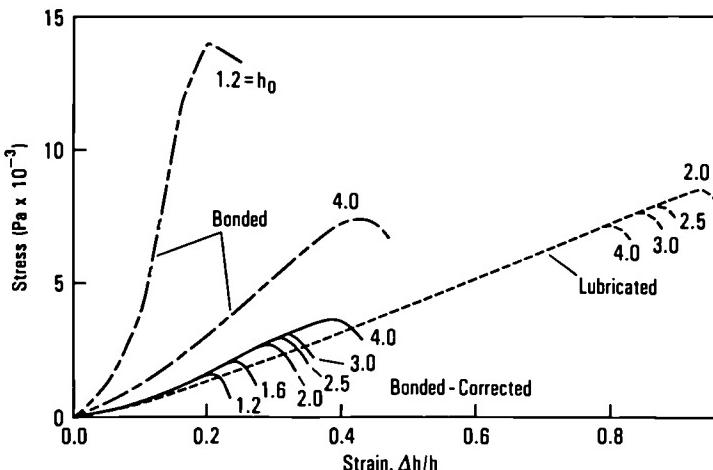


Fig. 3. Stress (σ_B , σ_{BC} and σ_L) versus strain curves for 10% wheat starch gels showing the agreement between the response in lubricated compression (σ_L) and the response in bonded compression corrected for shape change (σ_{BC}). The magnitude of the correction given by eqn. (9) is shown by the difference between the bonded and bonded-corrected plots. The difference in fracture behaviour under lubricated and bonded conditions is evident, the bonded-corrected fracture occurring at lower stress-strain levels than in lubricated compression (Christianson *et al.*, 1985).

coefficients suffice. In the materials examined by the author the frictional effects can exceed these limits and Mohamed's comment needs to be checked for each system examined. The advantage of bonding the sample to the platens is evident since the area of the sample in contact with the platens will then remain constant and the value of the coefficient of friction does not arise. Mohamed has also reported that it is easier to restrain the gel rather than attempt to ensure there is no friction between the gel and the platens, and that with air bubbles present Poisson's ratio will not be 0.5. This is a significant point, for which there seems to be little consideration in the literature. It means that the third strain invariant, I_3 (eqn. (3)), is not unity and the inclusion of a term involving I_3 in the strain energy function is necessary. Systems for which fuller investigation of volume effects might be warranted would be in the properties of bread and bread crumbs (Hibberd and Parker, 1985; Abu-Shakra and Sherman, 1984).

Fracture Effects in Different Testing Modes

The value of complementary experimental methods is also clear in work on complex gel systems, as in the studies of Montejano *et al.* (1983, 1984a,b).

They studied selected comminuted-muscle gels and egg-white gels. Compressional deformation experiments carried out by this group are routinely made with the sample/platen interfaces lubricated to ensure reproducibility. They were primarily interested in fracture behaviour under gross deformation as being of prime significance in food texture determination, a concept in agreement with Jowitt's (1979) comments. In comparing beef and pork gels in compression and torsion, they found true shear stress, strain and modulus in agreement at fracture. Such agreement was not found with turkey gels in compression and torsion experiments for reasons which are unclear but, perhaps, are related to the fact that turkey gels need particularly large strains for fracture and there were very large shape changes prior to failure. The combination of two measurements is nevertheless most informative and should lead to a greater understanding of the meaning and significance of the results of each experiment.

A second advantage of having alternative experimental procedures is illustrated by the results of Montejano *et al.* (op. cit.) with the surimi gels. In uniaxial compression tests, failure did not occur even at axial strains of up to 97%. Surimi gels did fail in torsion, however, so that this alternative testing method for fracture behaviour was available to them. Similarly, in the work illustrated by Fig. 3, fracture was not observed in lubricated compression at initial heights less than 2 cm but occurred for all samples, regardless of height, under bonded conditions.

The minimum requirements for any investigation of material properties are that (i) the results should be reproducible and (ii) material properties should be independent of testing mode and sample dimensions. That dimensions can play a significant role was emphasised recently by Chu and Peleg (1985), and even when empirical tests are used it is essential to be aware of the possibility of results being dependent on sample size. This is a particularly important consideration for heterogeneous composite systems. Even if the material is isotropic, the particle size of the filler should be small compared to the sample size. If the filled system or composite system is anisotropic, the problems are compounded because attention must be given to the sample orientation during measurement. Fracture behaviour can depend on sample dimensions (see Fig. 3), and this feature of mechanical behaviour of foods warrants further consideration.

COMPOSITE MATERIALS

Composite systems can include materials containing spherical or acicular fillers, or plate- or disc-shaped particles. Laminates, foams and honeycomb

Structures are other examples of composite materials. Many foods can be regarded as composites. Many of the relevant papers are in the polymer composites, mechanics, physics and engineering literature. Jowitt (1979) made a clear plea for fuller application of the concepts from these other fields to problems of characterising, processing and understanding foods. To review all the relevant literature would be an awesome task but a few examples of recent work relevant to foods may be helpful. The work of Wu *et al.* (1985) deals with the modification of surimi gels by adding starch particles as fillers. Sharma (1984) considered the general criterion for structural failure of biological materials. Holt and Schoorl (1982) pointed out the rôle of mechanical failure in fruits and vegetables in relation to damage in processing and handling and to characterisation of textural properties. They developed failure diagrams to provide 'a sound conceptual framework for investigations of the mechanics of failure of fruits and vegetables'. A constitutive relationship for apple cortex was developed by Datta and Morrow (1984), choosing the apple as a 'logical choice as a source for specimens representing a composite, nonhomogeneous and anisotropic biological material'.

A good introduction to composite behaviour is given by Nielsen (1974), particularly in Chapter 7, Volume 2, where Fig. 3 shows the effect of the volume fraction of filler particles on modulus as well as the effect of incorporation of air as filler (foams). One interesting section deals with errors in determining the moduli of composites. Nielsen notes that many results in the literature are in error because of skin effects. In tests such as torsion or flexion the properties of the surface are 'emphasized at the expense of the interior', a point which can be of particular concern in foods. Chapter 8 of Nielsen's Volume 2 deals with fibre-filled and other composites, the discussion again being very relevant to the characterisation of foods such as meats which have a grain.

Occasionally, papers appear which, while rather esoteric and apparently remote from food systems, may have application to them. Thus, Mecham *et al.* (1983) discuss the solid particulates formed in standard diametral and axial impact tests of small cylindrical specimens of glasses. A correlation was found between the size distribution, plotted as straight lines on log-normal coordinates, the resultant descriptive characteristics and impact severity for both crystalline and vitreous specimens. Certainly, it would be expected that the sensory perception of brittle foods would depend on particle size and size distribution produced during mastication and so the methods discussed by Mecham *et al.* may provide some insight into new approaches for treating and testing brittle foods.

Time Effects and Stress Relaxation

Materials classed as solids can show a wide range of time effects. Deformation of brittle foods may show little dependence on time, although the fracture properties of brittle materials may be dependent on rate of deformation. Other more complex foods in which rearrangement of structural units, cross-links, etc., may occur under stress or deformation will exhibit more marked time effects. Most solid food materials are biologically active (Peleg and Pollak, 1982), but the consequent time effects will not be considered here. Physical instability which occurs under stress or strain imposed on the material (so that mechanical equilibrium is not readily attained) is the subject of concern here. Such instability means that in deforming a sample, as in an Instron test, the stress-strain curve depends on time, and hence on the rate at which the sample is being deformed. Similarly, if a given strain is imposed on a sample, the stress decays with time (stress relaxation). Alternatively, if a given stress is imposed, the deformation changes with time, i.e. the material will creep. (See, for example, Mitchell and Blanshard (1976a,b).) It is sometimes difficult to distinguish a solid from a very high viscosity liquid,* but Peleg and Pollak (1982) remark that 'the mathematical distinction between solid and liquid is very clear. It reduces to the simple question of whether the stress of a deformed specimen approaches (though asymptotically) a zero or a finite level'. They go on to remark that it may be difficult to determine experimentally whether the infinite time stress is zero or not. For instance, doughs, which are classified as viscoelastic fluids, retain stresses in a relaxation experiment for as long as several hours. Doughs, as with other foods, have a very broad distribution of relaxation times and this is reflected in complex stress/time/strain relations.

In a stress relaxation experiment an instantaneous deformation is imposed on the material and the resultant stress is measured as it decays with time. There are a number of ways to treat such data. For example, Feltham (1955) shows that for a wide range of materials for which a log-

* It is futile to fret over whether a thing fits into only one or the other man-made category, particularly when such categories are defined in ways which are not mutually exclusive, as is often the case with definitions of 'solid' and 'liquid'. Although it is possible to define solid and liquid in ways which are less conducive to confusion or uncertainty than those which depend on a particular response to *stress* or *strain*—especially if they omit *time* from the definitions—it is possible to avoid such dilemmas entirely by referring to 'solid properties' or 'liquid properties' (or to 'elastic properties' or 'viscous properties') of materials and recognise that most materials—certainly most *food* materials—may, under appropriate conditions, possess either, or both.—Ed.

If normal distribution of Maxwell elements is assumed, probability plots can be used to characterise the relaxation process. Feltham also refers to early work in the polymer area on alternative methods of examining and analysing relaxation data.

For relatively solid materials there may be little time dependence but many foods, because of structural changes or rearrangement when strained, may show marked time effects. The question that arises about such material is how instantaneous can a deformation be? The assumption of an 'instantaneous deformation', a step-function strain, may not be a good one. This can be a particularly serious problem in the study of large deformation effects since the imposition of a large deformation is obviously more time-consuming than imposing a small deformation. How does the time to deform, t_1 , affect the relaxation curve? Although in principle the time t_1 can be made as small as is wanted, the resultant high deformation rate may break the sample, and there are always concerns about the response time of recorders and transducers or other deformation- and force-measuring devices. So, for solid food systems whose relaxation behaviour is significant, account must be taken of the effect of deformation time on the subsequent relaxation behaviour.

This is not an easy problem to deal with. If the material is described by an appropriate constitutive relationship, the required calculations can, in principle, be carried out; but such an equation is usually not available. For linearly viscoelastic materials, Meissner (1978) recently published a procedure. He suggests a simple procedure to obtain linear viscoelastic material functions for both polymeric solids and liquids which avoids the 'factor-of-ten rule' for short relaxation times. This author is not aware of any applications of this procedure to food materials, many of which are beyond doubt non-linear systems; in addition, the strains imposed are not imposed at a constant strain rate, one of the requirements of Meissner's method.

Peleg (1979, 1980b) and Peleg and Normand (1983) suggested representation of short-term relaxation data as

$$\frac{F(0)t}{F(0) - F(t)} = k_1 + k_2 t$$

where $F(0)$ is the force at time $t = 0$, $F(t)$ is the force at time t , and k_1 and k_2 are constants. This relationship has been used successfully by others, for example by Masi and Addeo (1984), in studies on mozzarella cheese. In systems to which the author has applied the procedure, the plots always show two regions of different behaviour, as is also the case with the

probability plots after Shelef and Bousoo (1964). Two sets of constants are therefore needed to describe the material by either of these methods. More significantly, the fitting terms are dependent on rate of testing, and so a degree of complexity is introduced which appears, in principle, to be related to the dependence of relaxation data on the time to deform. These types of plots are, nevertheless, worth examining, but to study the fundamental issue of the effect of deformation time other approaches appear to be necessary.

One method worth examining is an older procedure proposed by Zapas and Phillips (1971) and Zapas and Craft (1965). This work is an application of the Bernstein-Kearsley-Zapas incompressible elastic fluid theory and illustrates the use of the theory both in calculating stress/strain response for a number of simple extension histories from single-step relaxation data and procedures for comparing a material's responses after different deformation times. Their applications were to elastic fluids and rubber-like solids such as cross-linked elastomers and plasticised polyvinyl chloride. The author and his colleagues have carried out experiments on food systems for which the procedure seems applicable but the results are at a preliminary stage. It does seem, however, that the method is worth pursuing both for solid-like and semi-solid foods and for highly viscous and elastic systems such as doughs.

Friction

As discussed earlier, uniaxial compression of a food will give results which, in general (platen/sample interfaces neither bonded nor lubricated), will depend on both the frictional properties of the interface and the bulk properties of the material under test. While frictional effects can be eliminated (lubricated compression) or maximised (bonded), the frictional properties are important in affecting sensory effects in the mouth. The importance of frictional effects is recognised and has been discussed by Voisey and de Man (1976), Bourne (1976), Culoli and Sherman (1976) and Vernon Carter and Sherman (1978). The subject is also of significance to the polymer area, and attention can be drawn to the work of Gent (1974) and Gent and Henry (1982). Frictional effects must also be considered in food extrusion where some systems exhibit plug flow with the extruder output being determined by the coefficient of friction between the extruder metal and the food plug (Jasberg *et al.*, 1979). They have found a relationship between coefficient of friction and percentage moisture which is linear within the range from 10 to 40% moisture. Gent commented to the authors that this simple relationship was unexpected and raised concerns regarding

general problems in evaluating the coefficient of friction and the vital role played by total pressure and other variables which can significantly affect the results. Gent's concern is exacerbated in foods where mouth feel depends in part on frictional effects which in turn are modified by the presence in the mouth of saliva and by pressure and temperature.

CONCLUSIONS

The determination of the mechanical properties of solid foods is a difficult and demanding task for the food scientist because of complexity of food structure and composition. For brittle foods there are opportunities to apply concepts from the field of composite and polymeric materials as noted by Jowitt (1979). For softer solids frictional and relaxation effects deserve greater attention. Friction plays a significant rôle in compression testing and in texture profile analysis and is, therefore, a significant factor in evaluating sensory attributes of foods. Relaxation effects are difficult to ascertain, and more fundamental studies of testing rate and deformation time are necessary. Fracture behaviour, and particularly differences in fracture stress in different testing modes, deserves more attention. For brittle foods this would include size and shape distribution of the fragments after fracture.

More work on frictional effects in the mechanics of solid foods is indicated, but relatively little work is available. Attention can be drawn to a method proposed by Atkin and Sherman (1984), who examined the effect of sample diameter-to-length ratios and the resultant differences; where the D/L ratio increased, the relative effect of friction decreased. The observations may have implications for sensory evaluation of firmness.

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DISCUSSION

D. A. E. Ehlermann asked if Bagley's equations were appropriate to compare relaxation results from different laboratories using different deformation rates and, if the only instrument available were relatively slow-moving, could any information on high rates of shear be extracted from its results, e.g. in relation to chewing. *E. B. Bagley* reiterated that there was no problem in dealing with results from rapid deformation-relaxation tests. The direct results were valid. However, the deformation *history* of a slowly deformed specimen profoundly affected its relaxation behaviour and he did not think that results from such tests were of use in predicting the behaviour of the same material in relaxation after rapid deformation. Calculations would be more useful. *J. de Baerdemaeker* asked if the *failure* pattern of lubricated and non-lubricated samples was different, as the stresses might be greater locally in bulges and so the actual local failure stress might be the same in both cases. *Bagley* confirmed that there were differences, the bonded specimens appearing to fail in shear, the lubricated ones in tension of some form. This is illuminated by their preliminary work on specimens containing holes, a condition requiring further study.

H. Schubert asked how non-uniform materials should be dealt with. *Bagley*: *Inhomogeneous* materials should be tested in samples large enough for the scale of inhomogeneity to be small in comparison, so that the results were independent of sample size. *Anisotropic* materials, on the other hand, just had to be tested in the different directions in which the properties were different, in order to characterise the material completely. These were complex materials and had to be dealt with accordingly.

Overall Survey of the COST 90bis Work on the Solid Properties of Foods

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SUMMARY

An overall survey of the work of the COST 90bis subgroup on mechanical properties of foods is presented. Detailed analysis is given of the initial calibration exercise carried out by the group together with some details of the collaborative programme on food materials such as cheese, meat products, apples and gels. The collaborative experiments to develop simpler test methods for flow properties of powders is briefly described. A brief description of the work on preparation of a bibliography and data abstraction is given together with the recommendations of the group on the reporting of compression data with adequate contextual information. Finally, the areas which might be covered in a possible future collaborative study are outlined.

1. INTRODUCTION

In late 1982 the Council of the European Economic Community adopted a concerted action project on the effect of processing on the physical properties of foodstuffs and simultaneously approved a concertation agreement whose purpose was to enable the participation in the project of COST member countries who were not members of the EEC. In both documents, mechanical properties were defined as including density, porosity, stress, strain and fracture of integral solids and the mechanical properties of particulates such as powders and agglomerates. A footnote to all areas of intended study stated that the study was 'related to the intention to define general standard methodology taking into account the possible

influence of the different parameters'. Under a separate heading emphasis was placed on data collection (EEC, 1982).

Thus was defined the broad area in which the subgroup on mechanical properties could work and could be summarised as including all of the normally-accepted solid properties of foods with some emphasis to be placed on methodology and data collection.

Obviously, a small group working to a restricted timetable could not hope to cover all of the possible properties listed and so, of necessity, some selection of properties for study had to be made. A second logical reason for some selection or restriction of objectives is that without the interest of more than one country in a particular property, there cannot be a collaborative programme. One of the first decisions of the subgroup was therefore to confine attention to stress-strain relationships in solid foods and to consider some powder properties. Within both areas, methodology development and data generation would be given priority.

2. PROGRAMME EVOLUTION.

The work programme of the group covered several areas, each of which is described in some depth either below or in related chapters. Of necessity, only a small number of topics from the wide range of mechanical properties of foods could be selected for study by the group.

An early decision in the programme evolution was to include only well-defined solid properties of foods, to confine the study to fundamental engineering properties and to exclude deliberately the wide range of specifically textural attributes from the preliminary work. (The extensive field of texture studies could form a very useful extension of the current work within a new project.) Consequently, force-deformation studies were selected for collaborative study and, in order to minimise problems of sample fixing and to be able to work within the normal range of instrumentation, compression testing was chosen.

Subsequent to this basic decision, a work programme quickly evolved and can be summarised as follows:

- (a) A 'participant calibration' exercise.
- (b) Testing of selected solid foodstuffs, including evolution of test procedures.
- (c) Relaxation studies on foods and their interpretation.

- (d) Development of test procedures for powdered and agglomerated foods.
- (e) Preparation of a bibliography of mechanical properties of foods and the abstraction of data from the constituent publications.

3. CALIBRATION EXERCISE

As a wide variety of test instruments was available within the participating laboratories, a simple standardisation exercise was proposed. Rather than adopt the convention of using test samples of standard rubbers or of using calibrated springs, it was decided that the use of nominally identical food materials would be preferable in this food-related project.

The materials chosen were two types of mint-flavoured sucrose-based sweets, one being 'POLO' mints chosen for their annular or 'proving-ring' shape, the other 'SILVERMINTS' being representative of the flat disc mint commonly available throughout Europe under different brand names. These were distributed from Dublin.

For both varieties of sweet it was decided that compression to fracture would be undertaken vertically along a diameter at a compression rate of 1 mm min^{-1} (or as close to 1 mm min^{-1} as was available on the particular instrument). Because of the difficulties of shape, it was decided that only fracture force would be recorded.

Statistical analysis of the results was carried out according to the procedure used in a previous collaborative exercise within COST (Spiess and Wolf, 1983). This procedure consisted of four steps:

- (a) Grubb's test for the identification and elimination of outliers within individual experimental data sets.
- (b) Comparison of variances by Bartlett test.
- (c) Identification of systematic deviations.
- (d) Calculation of mean value and standard deviation.

A subsequent and, as will be shown, less-successful phase of this exercise was the distribution and testing of both polystyrene and gelatine cylinders. The polystyrene samples were cylinders of diameter 35 mm and height 50 mm cut from an expanded product whereas the gelatine samples were cylinders of diameter 25 mm and height 35 mm formed from solutions of gelatine of Bloom number 260.

3.1 'POLO' Mints: Results

The results from the participating laboratories are shown in Table 1. Not all laboratories were able to achieve compression rates as low as 1 mm min^{-1} and not all samples survived the air-mail distribution process. One laboratory replaced the damaged samples with their locally-purchased equivalent but as these were from neither the same batch nor the same manufacturing plant, real differences were to be expected. The low results obtained by another laboratory with some broken samples suggest that the remaining, apparently undamaged, specimens used had, in fact, microscopic imperfections before testing. Between the remaining laboratories

TABLE 1
FORCE REQUIRED TO FRACTURE 'POLO' MINTS

Laboratory number	No. of samples	Compression rate (mm min^{-1})	Outliers eliminated	Force for fracture mean (N) with standard deviation
9	9	1	none	73.97 (7.30)
10	27	1	none	69.05 (9.91)
8	12	1	none	72.17 (8.73)
8	15	1	none	82.97 (10.79) ^a
6	16	1	none	69.01 (10.91)
7	9	1	none	76.44 (10.84)
3	13	5	none	68.32 (9.60)
2	13	5	none	83.38 (8.28) ^b
13	15	5	1	69.10 (6.99)
6	15	5	none	61.08 (12.41)
11	16	5	none	34.80 (6.14)
8	10	10	none	84.41 (12.52) ^{a,c}
11	12	10	1	16.97 (2.43)
8	15	20	none	84.35 (6.46) ^{a,c}
12	11	50	1	12.12 (2.80) ^b
12/repeat	9	50	2	21.09 (1.39) ^b
13	17	50	1	18.38 (6.10)
7	9	50	none	56.89 (11.23)
Between lab. comparisons		1		73.94 (4.82)
		5		70.94 (8.08)
		> 5		no analysis possible

^aLocally purchased samples.

^bDamaged in transit.

^cComputer collection of data.

See Table 6 for laboratory codes.

there was good agreement, the between-laboratory standard deviation being less than those within individual laboratories, with the indication that the instruments were in good agreement.

In addition, the differences between the 1 mm min^{-1} and 5 mm min^{-1} compression tests were not significant.

It also appears that many instruments have recording devices with response rates too slow to follow the failure of brittle materials such as the mints in question. This is particularly apparent from the results for high compression rates (i.e. the recording pen proved too slow to follow the rapid rate of force increase before fracture). Computer collection of data can eliminate this problem.

3.2 'SILVERMINTS': Results

With 'SILVERMINTS' there was again good agreement when similar compression rates were used. Table 2 summarises the results obtained.

Several different failure patterns were noted for these disc-shaped sweets: single, central, vertical crack (Fig. 1a); a vertical crack on each side of the

TABLE 2
FORCE REQUIRED TO FRACTURE 'SILVERMINTS'

Laboratory number	Number of samples	Compression rate (mm min^{-1})	Outliers eliminated	Force for fracture mean (N) with standard deviation
10	11	1	none	321.95 (29.71)
8	12	1	none	334.96 (30.72)
6	11	1	1	312.94 (19.01)
7	10	1	none	323.50 (44.35)
3	10	5	1	317.12 (44.08)
2	10	5	none	350.20 (28.17)
6	5	5	none	333.34 (34.36)
12	15	50	1	396.16 (30.59)
13	16	50	none	374.38 (63.69)
7	5	50	none	327.00 (80.05)
6	4	50	none	313.68 (58.13)
Between lab. comparisons		1		323.33 (7.83)
		5		333.55 (13.51)
		50		357.81 (33.70)
		all rates		336.84 (25.43)

See Table 6 for laboratory codes.

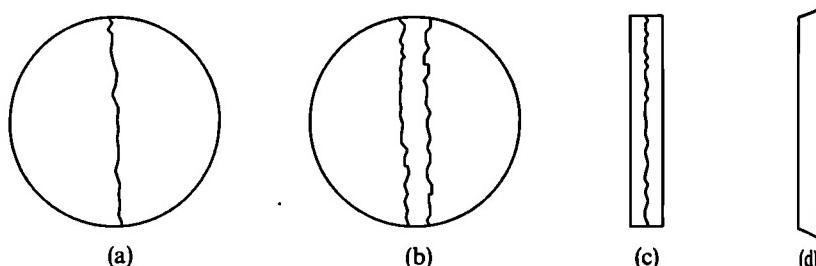


Fig. 1. Fracture patterns for disc-shaped sweets. (a), central fracture; (b), twin fractures with central pillar; (c), twin discs; (d), actual side profile.

centre line leaving an intact pillar (Fig. 1b); and finally, fracture of the disc into two thinner flat discs (Fig. 1c). This last was probably due to slight tapering of the sides of the sweet mould resulting in compression as shown in Fig. 1d.

An additional problem with these materials is their hygroscopic nature. Exposure to high humidities results in rapid moisture uptake and can change the mechanical properties of the samples.

Despite these minor difficulties there was ample evidence that the participants' measurements were in very good agreement and that work mutually interchangeable between laboratories was possible.

3.3 Polystyrene Cylinders: Results

The expanded polystyrene cylinders did not fracture but spread laterally between the compressing platens. Consequently, the force required for a

TABLE 3
FORCE REQUIRED FOR 25% COMPRESSION OF EXPANDED POLYSTYRENE CYLINDERS
(35 mm diameter, 49 mm high)

Laboratory number	Number of samples	Compression rate (mm min^{-1})	Outliers eliminated	Force for 25% compression mean (N) with standard deviation
7	10	1	none	77.7 (0.63)
6	5	5	none	93.70 (3.85)
8	4	5	none	104.52 (2.799)
9	5	5	none	120.36 (5.69)
10	10	5	none	95.25 (1.69)
12	5	50	none	122.57 (5.63)

See Table 6 for laboratory codes.

TABLE 4
FAILURE FORCE FOR CYLINDERS OF GELATINE GEL
(25 mm diameter, 25 mm high)

Laboratory number	Number of samples	Compression rate (mm min ⁻¹)	Outliers eliminated	Failure force mean (N) with standard deviation
7	8 ^a	1	one	2.49 (1.10)
6	3	5	none	7.55 (2.65)
8	8	5	none	11.81 (2.34)
9	8	5	none	9.49 (2.13)
6	4	10	none	7.59 (2.62)
12	7	50	none	19.52 (5.02)
13	5	50	none	16.90 (3.14)

^aDamaged samples.

See Table 6 for laboratory codes.

25% compression was recorded and compared. A summary of results is given in Table 3. It has been suggested that the absence of temperature control during testing could have affected results due to the relatively high temperature coefficient of stiffness of polystyrene.

3.4 Gelatine Cylinders: Results

For gelatine gels very few results were available due to deterioration of the preformed samples (25 mm diameter, 25 mm high, Bloom number 260) in transit. It is possible that this was due to adverse conditions, including large temperature variations and possible freezing, during their air transport. Two laboratories tested undamaged samples but as one used non-slip platens and the other lubricated platens, no direct comparison is possible. Results are summarised in Table 4.

4. TESTING OF A RANGE OF SOLID FOODS

Following on the calibration exercise the collaborative trials were extended to solid foodstuffs. Of necessity, the selection had to be somewhat restricted and was made on the basis that the examples chosen were representative of a wide variety of foods and should also be amenable to distribution without deterioration. Some Cheddar cheeses from the UK and a 'pasta filata' cheese, 'Silano', from Italy were chosen as dairy commodities; two canned

meats, a luncheon sausage and a chopped ham were selected; 'Golden Delicious' apples were chosen from among fruits and vegetables, and agarose gels were selected as model food systems.

It was apparent from the earlier calibration trials that the test methods had to be specified in precise detail to ensure comparability of test results from different laboratories. However, as it was not known in advance exactly what all the factors were which would or would not affect comparability, it was agreed that detailed contextual data should be gathered at the time of each test. Experts in each commodity area undertook the development of detailed test specifications for each commodity type and these are described in other chapters.

For these tests the compression rate adopted was 5 mm min^{-1} as this appeared to be the most commonly-available lower speed on the test instruments of the participating laboratories. Sample size varied according to the test specification but in most cases they were either prisms $20\text{ mm} \times 20\text{ mm} \times 30\text{ mm}$ or cylinders of diameter 17 mm and height 17 mm. Compression to failure was carried out at room temperature using non-slip platens.

The following results were abstracted from the recorded data:

- (1) Stress at failure (as most of these materials changed shape during compression, this stress was calculated on the original cross-sectional area of the sample).
- (2) Strain at failure.
- (3) Apparent elastic modulus (as very few foods exhibit true elastic deformation but give curved rather than linear force-deformation plots, it was agreed that the slope of the middle third of the deformation plot would be used in assessing this quantity).
- (4) Failure energy.

Statistical analysis of these quantities was similar to that previously outlined.

Additionally, laboratories with suitable equipment were asked to carry out stress relaxation tests on the samples.

4.1 Cheese Tests

The detailed methodology and the test results for the compression tests on the three cheese samples are given in Chapter 31 by Masi including detailed discussion of the selection criteria for the test operating conditions together

with details on the preferred method of analysis of both the force-compression curve and that of the stress relaxation experiments.

Whilst detailed discussion is left to Chapter 31, it can be noted in this general review that the close agreement between results for one of the cheeses reconfirmed the conclusion of the calibration exercise that given the same materials, and clear definition and control of test condition, collaborative tests of this type are capable of close corroboration over short periods of time.

4.2 Meat Tests

As there is no separate chapter on the measurements on the meat products, the results of the collaborative experiments will be presented here.

Two examples of commercial canned meat products were chosen for examination, one a finely-commminuted pork sausage type material (Prince's Pork Meat), the other a similarly-shaped comminuted product having some larger meat particles (Spam). Both materials were distributed from the UK to the eight laboratories which participated.

As the meat and the cheese were mechanically similar examples identical test procedures were used for both. The specified test piece was a prism 20 mm × 20 mm × 30 mm high or, if cutting equipment of suitable accuracy and rigidity for this could not be obtained, a cylinder 17 mm diameter by 17 mm high was used. The samples were first allowed to attain room temperature and were then compressed to failure between rough platens at a compression rate of 5 mm min⁻¹.

From the force-displacement curves the four quantities: stress at failure, strain at failure, apparent elastic modulus and energy to failure, were derived and sent to the author for collation together with the original test results. The results are presented graphically in Figs. 2-5. In these figures the mean and a band of plus and minus one standard deviation is shown for each set of tests.

As was expected, the scatter of results was greater for 'Spam' with its greater particle size and size range than for the Pork Meat. This is particularly evident in Fig. 2 where yield stress results are summarised. There are two quite distinct sets of results for the Pork Meat, three laboratories returning results approximately double those of the other five laboratories. This is believed to be a real difference between the cans of meat sent to these two groups of laboratories as the same differences were not apparent with Spam nor, indeed, with any of the other collaborative trials. An interesting feature of this experiment is that despite real differences in yield stress, little variation was observed in yield strain. Consequently,

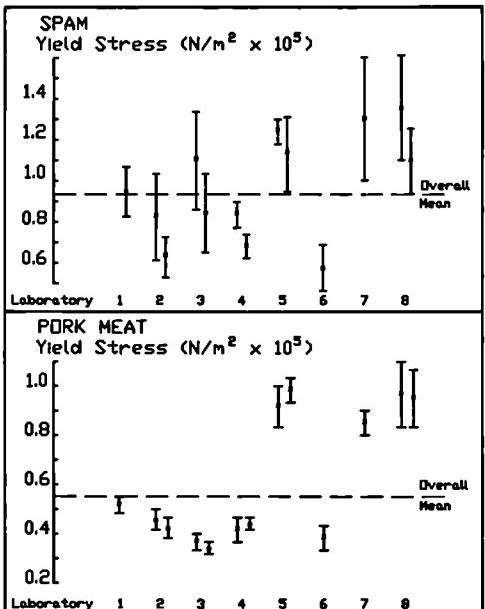


Fig. 2. Yield stress for meat products. Means and standard deviations of results from each laboratory.

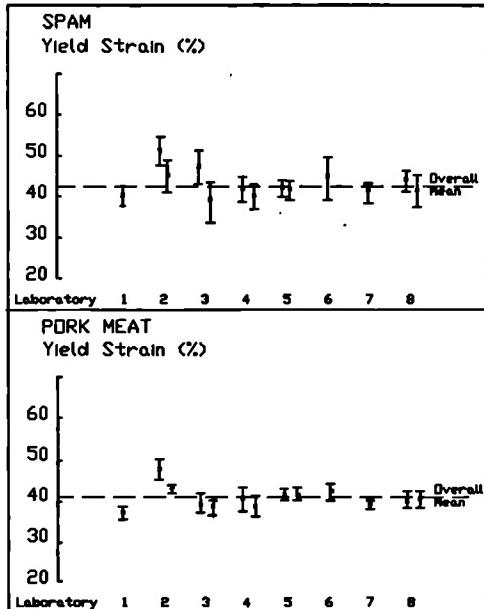


Fig. 3. Yield strain for meat products. Means and standard deviations of results from each laboratory.

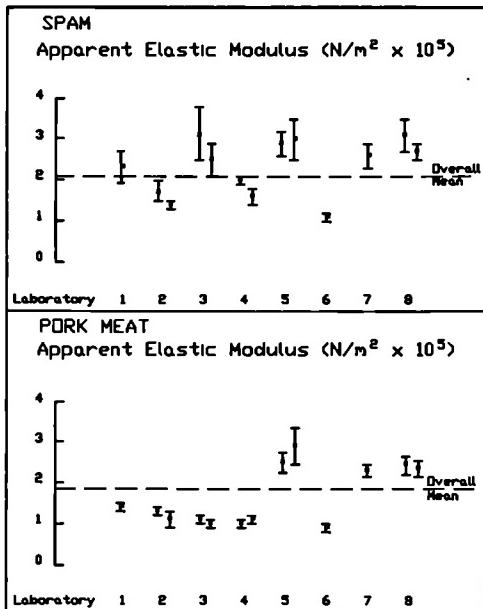


Fig. 4. Apparent elastic modulus for meat products. Means and standard deviations of results from each laboratory.

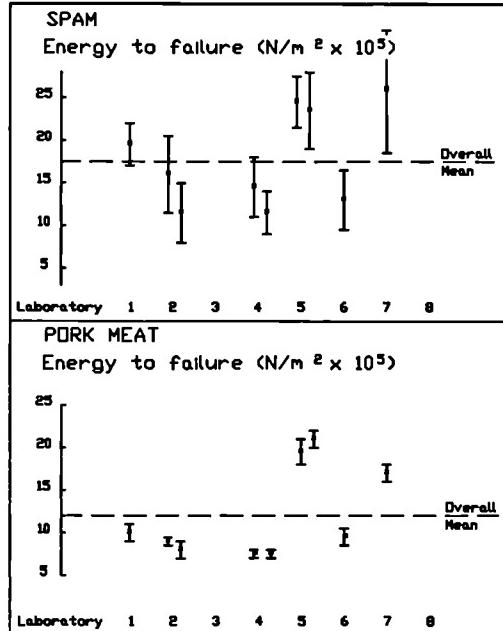


Fig. 5. Energy to failure for meat samples. Means and standard deviations of results from each laboratory.

similar patterns are evident for the remaining two properties, elastic modulus and failure energy, as those for yield stress. While this grouping is clearly visible for the Pork Meat results, analysis of variance shows different groupings for the Spam results with three sets of results significantly lower than the remainder.

4.3 Apple and Agarose Gel Testing

The methodology and results for apple testing are given in Chapter 32 by de Baerdemaeker *et al.* while those for agarose gels appear in Chapter 34 by Durà *et al.* In the case of apples, participants were asked to test locally-purchased samples of the variety 'Golden Delicious'. For the agarose gels, samples of agarose (Sigma Chemicals, Type 1, low EEO) were distributed from a common source together with detailed instructions on the sample preparation and test methodology.

5. POWDERS AND AGGLOMERATES

A separate collaborative exercise carried out on powders and agglomerates, detailed in Chapter 35 by Ehlermann and Schubert, was undertaken in pursuit of a simple method for determining some of the flow properties of powders from a compression test using a cylinder and piston test cell incorporated into standard, widely-available force-deformation test equipment. Reliable data in this subject had hitherto necessitated the use of the complex (and expensive) Jenike shear cell. Some work by Peleg *et al.* had suggested that close correlation could exist between such data and the simple compression test.

6. RELAXATION STUDIES

As many of the participants had the capability of carrying out stress-relaxation tests, such tests were incorporated into the compression trials wherever possible. Analysis of relaxation data presents many difficulties as in all cases models are used to approximate the curve and the accuracy of selection or derivation of the model equations will influence the subsequent usefulness and accuracy of the model chosen. Stress relaxation in cheese and apples are dealt with in the respective chapters and recommendations

on the interpretation and analysis of relaxation data are detailed in Chapter 36 by Launay and Cantoni.

7. BIBLIOGRAPHY AND DATA COLLECTION

In addition to the collaborative experiments, the group undertook the preparation of a bibliography and the abstraction of mechanical property data from the original papers to form the basis of a data bank. Both exercises formed part of the collaboration with the Subgroup on Physical Property Data. The bibliography was prepared with the help of computer searches of standard literature data bases followed by examination of the individual items to ensure their relevance.

Data abstraction from this literature and an associated exercise in data generation and collection from within individual laboratories formed the most controversial aspect of the group's work. There was a strongly-held view within the group that unless data had been generated using test conditions similar to those for its eventual use, its value was considerably diminished and, indeed, its relevance doubtful. Another view within the group was that, until more is known of the influence of context it is not possible to generalise and the more data there are to be studied the more we can learn about this and other aspects. Further, for the present, in many cases, approximate data are preferable to no data at all and the availability of at least some data enables the small processor without test facilities to improve on the 'educated guess' that might otherwise be his only resort.

TABLE 5
INFORMATION TO BE INCLUDED IN COMPRESSION TEST REPORTS

<i>Contextual information</i>	<i>Measurement conditions</i>	<i>Results</i>
1. Detailed description of sample 2. Sample dimensions 3. Sample history (including preparation and conditioning)	1. Temperature of environment 2. Relative humidity of environment 3. Sample temperature 4. Interface between sample and compression surfaces (a) Material (b) Roughness (c) Dimensions 5. Compression rate 6. Machine details Accuracy of (a) compression rate, and (b) force measurement 7. Initial position of crosshead in relation to the sample 8. Response time	1. All original and derived results 2. Complete force deformation curve

Consequently, it was agreed, by some participants, to proceed with data abstraction from the literature and with data generation. This is still in progress and will be published in due course.

At an early stage in this work it became apparent that there was a very wide diversity in the test conditions used and that in many cases there was inadequate contextual data relating to the tests. Consequently, consideration was given to preferred forms of reporting and to itemising the information which should always be included. These are listed in Table 5. It was agreed that to facilitate comparison of results there should be some standardisation of sample size and that, in addition to the chosen compression rates, a rate of 5 mm min^{-1} should be included as a reference rate. The recommended sample size was that used in the collaborative studies, namely cylinders of 17 mm diameter and 17 mm height or prisms of 20 mm \times 20 mm \times 30 mm high.

8. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

8.1 Conclusions

Several objectives have been achieved within the limitations of the project. On compression testing, methodology has been refined for several ranges of food commodities and some guidelines on the interpretation of the output from force-displacement instruments have been prepared. In addition, some consideration has been given to interpretation of stress relaxation measurements. Methodology on the flow properties of powders has been developed and should in the longer term be of considerable benefit to the designers of storage and dispensing equipment for particulates. Finally, a start has been made on the preparation of a data bank on mechanical properties of foods and guidelines have been drawn up specifying the contextual information required to enhance the usefulness of such a database.

8.2 Recommendations for Further Work on Mechanical Properties of Foods

The members of the group devoted some time to discussion of the further studies necessary in the area of mechanical properties. In common with the recommendations of the other subgroups, these can be summarised as:

1. Collection of physical properties data on foodstuffs.
2. Contextualisation of physical properties data.

3. Application of physical properties data in food technology and engineering.
4. Correlation of physical properties data with sensory and quality attributes of foods.

Of these, two justify particular comment in relation to mechanical properties. The first is the contextualisation of mechanical properties data. The purpose of this important and much neglected area is to determine the degree of sensitivity of the common mechanical properties data to contextual factors likely to vary in normal circumstances. Within the scope of this exercise would be many of the items noted in Table 5.

The second is the correlation of physical property data with sensory and quality attributes of foods. This is particularly relevant in the area of mechanical properties. Examination of the literature on mechanical

TABLE 6
LABORATORIES PARTICIPATING IN THE COLLABORATIVE STUDY

<i>Code</i>	<i>Laboratory</i>
1.	Sprenger Institute, Wageningen, The Netherlands
2.	Technical University of Denmark, Lyngby, Denmark
3.	Agrochemical and Food Technology Institute, Valencia, Spain
4.	National Institute for Research in Dairying, Reading, UK (now the Food Research Institute, Reading)
5.	Dept. of Chemical Engineering, University of Naples, Naples, Italy
6.	Dept. of Agric. & Food Engineering, University College Dublin, Dublin, Ireland
7.	SIK—The Swedish Food Institute, Gothenburg, Sweden
8.	Dept. of Agricultural Engineering, Catholic University of Leuven, Belgium
9.	Dept. of Agricultural Mechanisation, Polytechnical University, Madrid, Spain
10.	Norwegian Food Research Institute, Aas-NLH, Norway
11.	Swiss Federal Institute of Technology, Zurich
12.	Refrigeration Institute, University of Madrid, Spain
13.	Agricultural Research Institute, Castleknock, Dublin
14.	Poultry Research Institute, Spelderholt, The Netherlands
15.	Federal Research Institute for Nutrition, Karlsruhe, Germany
16.	Food Research Institute, Norwich, UK
17.	Department of Food Science, University of Nottingham, Sutton Bonington, UK
18.	Ministry of Agriculture, Fisheries and Food, London, UK
19.	ENSIA, Massy, France
20.	Queen Elizabeth College, London, UK

properties reveals that much of the published data are not of a fundamental nature but merely an instrumental measurement which has been found to correlate to some degree with a desired sensory attribute. Such numerical data are useful sensory correlates but are of little use in fundamental understanding or in design or other engineering calculations. Detailed work is necessary if more basic mechanical properties are to be substituted with advantage for such empirical sensory correlates.

Rapid implementation of these recommendations is urgently required for the benefit of the food industry.

ACKNOWLEDGEMENTS

A programme such as outlined in this chapter would not have been possible without the support and willing participation of the many members of the COST 90bis Mechanical Properties Subgroup and the collaboration of the laboratories and organisations listed in Table 6, towards this advancement of knowledge. To all of these our grateful thanks.

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31

The Collaborative Compression Tests on Cheeses

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SUMMARY

Collaborative measurements of mechanical properties of Cheddar cheese and of Silano cheese are reported and discussed. They were part of a research project whose objectives were to establish the comparability of measurements in different laboratories and to identify the most suitable measurement conditions to generate reproducible mechanical data on cheese. The influence of some factors on the mechanical behaviour of cheeses is also examined and briefly reviewed.

1. INTRODUCTION

Mechanical properties of solid cheeses are commonly derived from force-compression curves generated from a range of test instruments, e.g. the Instron universal testing machine. Unfortunately, uniaxial compression of cheeses has often proved difficult to interpret in fundamental terms. Part of this difficulty arises from the fact that the response of these materials under uniaxial compression depends in general on the bulk material properties and on the conditions under which the test is run. In fact, since cheeses exhibit viscoelastic behaviour, their mechanical response depends on the relaxation phenomena which occur during the loading cycle and thus on the rate at which the sample is strained (Shama and Sherman, 1973; Peleg, 1977). In addition, since the samples may adhere to some extent to the moving parts of the equipment, the stress distribution during the loading is not uniform within the sample (Hammerle and McClure, 1971). Consequently, the resulting force-compression curves vary with the sample

size (Von Sachs, 1924) and with the contact conditions at the sample-machine interfaces (Vernon Carter and Sherman, 1978).

Usually test conditions have been selected at random and thus most of the data reported in the literature are not directly comparable. Further, comparison may be precluded by a lack of information on the sample history and the measurement conditions.

To avoid that and to promote the generation of comparable data among food scientists and technologists, the COST 90bis Mechanical Properties Subgroup developed a collaborative experiment in which 12 laboratories from eight European countries participated. The objectives were as follows:

- To establish the precision of measurement within and between laboratories.
- To select appropriate measurement conditions.
- To identify the most important contextual factors which may affect results.

2. MATERIALS AND METHODS

2.1. Food Materials

Three different cheeses were distributed to the participating laboratories:

1. Silano cheese, supplied by Latte Sud Matese, Caserta, Italy.
2. Sliceable processed cheese, supplied by Food Research Institute, Reading (FRIR), UK (previously known as NIRD).
3. Spreadable processed cheese, supplied by Food Research Institute, Reading, UK.

The samples of Silano cheese, having a cylindrical shape and a weight of 300 g, were prepared from a single batch. To avoid drying out, each sample was coated in paraffin and sealed under vacuum in a plastic bag. They were sent to the participant laboratories by air mail, protected in a polystyrene foam box. Only the sample received by Lab. 2 arrived with some evidence of spoilage.

Two blocks of sliceable processed cheese and two blocks of spreadable cheese were specially prepared, at FRIR, for this collaborative exercise. The blocks were cut into 20 parts of approximately 250 g each. One sample from each block was selected at random and sent by post to each of the participating laboratories.

2.2. Methods

Compression tests were carried out at room temperature at a constant cross-head speed of 50 mm min^{-1} . Sample shape and dimensions were not the same for all laboratories (Table 1).

The samples, on receipt, were to be stored in a refrigerator and brought to room temperature at least 1 h before the test. However, Labs. 1 and 5 performed the compression tests on Silano cheese specimens extracted from the refrigerator just prior to the test, and therefore tested at a temperature which, although unknown, was presumably between 4 and 6°C.

TABLE 1
DIMENSIONS AND SHAPE OF THE SAMPLES USED IN
COMPRESSION TESTS

Laboratory	<i>Prisms (cm)</i> $2 \times 2 \times 3$	<i>Cylinders (cm)</i>	
		<i>D</i>	<i>h</i>
1	✓		
2	✓		
3	✓		
4		1.7	1.7
5	✓		
6	✓		
7		2.16	3.09
8	✓		
9	✓		
10	✓		
11		1.68	2.30

For each cheese the following properties were determined from the force-displacement curve:

- yield or rupture stress;
- yield or rupture strain;
- modulus of elasticity; and
- yield or rupture work per unit of volume.

As the samples changed shape during deformation, stress and strain at any point were evaluated from the cross-sectional area and the length of the undeformed sample.

3. RESULTS AND DISCUSSION

3.1. Silano Cheese

The mean value and the coefficient of variation of the stress (σ_y) and strain (ϵ_y) at yield, the modulus of elasticity (E_{app}) and the corresponding work per unit of volume (W) as measured by each laboratory are summarised in Table 2. The results are listed in order of testing date.

Statistical analysis of the results summarised in Table 2 has shown that, when the results of Labs. 1 and 5 are omitted, the standard deviations between laboratories are similar to those within each laboratory.

The differences which exist between the results of Labs. 1 and 5 and those of the other collaborating laboratories can be attributed to the differences

TABLE 2
MECHANICAL PROPERTIES OF SILANO CHEESE

<i>Laboratory</i>	<i>Number of samples</i>	σ_y ($N m^{-2} (10^5)$)		ϵ_y (%)		E_{app} ($N m^{-2} (10^5)$)		W ($N m^{-2} (10^4)$)	
		Mean	SD %	Mean	SD %	Mean	SD %	Mean	SD %
5	9	0.48	10	47	8	1.49	8	1.31	9
3	5	0.23	13	31	13	1.01	40	4.88	15
4a	9	0.18	11	36	8	0.52	19	3.51	6
4b	8	0.13	8	39	5	0.36	8	2.93	12
2	10	0.17	12	27	8	1.09	17	—	—
1	4	0.50	16	37	1	2.67	15	1.54	13
6	3	0.18	11	30	0	0.66	10	3.09	11
7	5	0.31	13	43	2	0.85	8	3.20	22
8	11	0.56	8	35	2	3.64	10	—	—

in the sample temperature. In fact, in the case of Labs. 1 and 5 the temperature of the sample was probably between 4 and 6°C, while in all the other cases the temperature of the sample was in the range 16–24°C.

Samples of different age exhibit almost the same behaviour, as might have been expected, since they were coated with paraffin and sealed under vacuum in plastic bags. This double protection reduces moisture variation, which is the main factor affecting the mechanical behaviour of this type of cheese (Masi and Addeo, 1986). Only the samples examined by Labs. 8 and 9 differ from all the others in strength. However, it is noteworthy that while most samples were tested at an age of between 2 and 6 weeks, those tested at Labs. 8 and 9 were about 6 months old.

TABLE 3
MECHANICAL PROPERTIES OF SLICEABLE ENGLISH CHEESE A1

Laboratory	Number of samples	σ_y ($N m^{-2} (10^5)$)		ϵ_y (%)		E_{app} ($N m^{-2} (10^5)$)		W ($N m^{-2} (10^4)$)	
		Mean	SD %	Mean	SD %	Mean	SD %	Mean	SD %
11	—	0.97	—	30	—	—	—	—	—
7b	4	1.04	4	26	4	5.75	5	12.95	1
6	6	1.06	5	28	4	—	—	16.42	8
7a	4	1.07	9	26	8	6.59	7	12.36	22
4	10	0.99	7	20	4	6.12	13	11.43	10
3	4	0.77	3	25	5	4.02	5	11.20	6
10	—	0.95	—	26	—	5.20	—	14.5	—
1	4	1.20	8	28	8	8.19	10	19.58	1
2	6	0.98	6	31	5	3.96	16	—	—
8	7	1.44	5	28	7	9.19	9	—	—
5	5	1.42	8	23	12	5.32	15	11.40	7
9	5	1.56	7	41	8	5.87	15	11.24	17

3.2 English Cheese

Tables 3–6 show the mechanical properties of the English cheeses, while Figs. 1–4 show the sample location in the block from which they were cut. The results group the peripheral samples and the internal ones.

Again the results appear quite uniform in general, the data of all laboratories show that the sliceable cheese is stronger than the spreadable cheese and that one of the blocks of sliceable cheese was stronger than the other, while no difference exists between the two blocks of spreadable cheese.

TABLE 4
MECHANICAL PROPERTIES OF SLICEABLE ENGLISH CHEESE A2

Laboratory	Number of samples	σ_y ($N m^{-2} (10^5)$)		ϵ_y (%)		E_{app} ($N m^{-2} (10^5)$)		W ($N m^{-2} (10^4)$)	
		Mean	SD %	Mean	SD %	Mean	SD %	Mean	SD %
1	4	0.75	1	38	11	2.68	9	12.91	5
7a	4	1.06	6	—	—	—	—	—	—
8	8	1.39	9	24	2	10.00	11	—	—
11	—	0.68	—	35	—	2.27	—	—	—
7b	5	0.78	3	28	7	3.79	8	11.05	7
10	—	0.80	—	27	—	3.90	—	13.00	—
5	5	0.90	11	28	10	4.86	5	13.82	11

TABLE 5
MECHANICAL PROPERTIES OF SPREADABLE ENGLISH CHEESE B1

Laboratory	Number of samples	σ_y ($N m^{-2} (10^5)$)		ε_y (%)		E_{app} ($N m^{-2} (10^5)$)		W ($N m^{-2} (10^4)$)	
		Mean	SD %	Mean	SD %	Mean	SD %	Mean	SD %
7a	3	0.28	14	23	9	1.85	21	3.37	6
5	5	0.53	5	35	6	2.05	10	6.07	13
12	5	0.46	4	46	4	1.39	2	3.69	9
1	2	0.25	25	21	3	1.90	25	2.85	20
10	—	0.20	—	25	—	1.25	—	3.00	—
6	4	0.15	13	21	2	0.99	18	1.86	21
2	8	0.21	15	20	4	1.21	15	—	—
7b	4	0.29	14	24	4	1.78	7	3.53	14
8	7	0.33	15	17	15	2.96	23	—	—
3	6	0.35	20	26	7	1.74	18	5.22	28
4	5	0.29	10	19	3	2.05	6	3.33	8
11	—	0.32	—	22	—	—	—	—	—

There is an effect due to sample position within the main block: the behaviour of the sample taken from regions close to the surface is slightly different from that cut from the interior of the block. The effect of position appears to be much more evident in the spreadable cheese than in the sliceable one.

3.3. General Remarks

Standard deviations of the measurements on processed English cheese were generally smaller than those for Silano cheese. This is consistent with the fact that processed cheeses are more homogeneous than traditional cheeses.

TABLE 6
MECHANICAL PROPERTIES OF SPREADABLE ENGLISH CHEESE B2

Laboratory	Number of samples	σ_y ($N m^{-2} (10^5)$)		ε_y (%)		E_{app} ($N m^{-2} (10^5)$)		W ($N m^{-2} (10^4)$)	
		Mean	SD %	Mean	SD %	Mean	SD %	Mean	SD %
6	6	0.28	18	29	10	1.24	16	4.83	25
11	—	0.33	—	31	—	—	—	—	—
8	7	0.39	13	18	15	3.93	21	—	—
10	3	0.25	8	31	0	1.06	10	4.30	0
7a	5	0.35	9	30	7	1.65	12	4.92	11
5	5	0.30	7	32	30	1.58	27	3.23	44
7b	4	0.35	9	28	7	1.81	6	5.02	11

11		7 b	6
2			7 a
	8	5	4
		9	3
1			10

Fig. 1. Location of samples in the block of sliceable English cheese A1.

	7 a			
		.		
S				
P	11	7 b	10	
a	5		6	4
r			8	
e				

Fig. 2. Location of samples in the block of sliceable English cheese A2.

For each set of data the standard deviation in the yield stress was almost equal for all the laboratories. Nevertheless, large differences existed between standard deviations for modulus of elasticity and yield strain. However, the absolute values of the standard deviations were relatively small. This can be taken as evidence that in general mechanical data for these cheeses are quite reproducible.

The large scatter of results for strain and elasticity on Silano cheese is probably due to the shape of its compression curve. In fact, the compression

7a		5	9
7b	8		
		3	1
	11	4	10
	2		6

Fig. 3. Location of samples in the block of spreadable English cheese B1.

curve of this cheese does not show a well-defined yield point, but instead has a flat plateau with a gradual inflection. The identification of the yield point therefore often proved quite arbitrary. In addition, the region of perfectly elastic behaviour, i.e. the range over which the force increases linearly with the deformation, is very short or does not exist at all. This, of course, makes questionable the measurement of an elastic modulus. On the other hand, the shape of the force-deformation curves for the English cheese, shown in Fig. 5, causes little uncertainty in evaluating its mechanical properties.

	6	11		
S	5			8
p				
a				
r			7 b	
e	7 a		10	

Fig. 4. Location of samples in the block of spreadable English cheese B2.

At the end of this brief analysis, it can certainly be concluded that this concerted action has been successful and that all the aims pursued have been achieved. In fact, most of the differences between laboratories were small or could be explained by differences in the contextual factors which varied from one to another. Moreover, the emergence of a statistically validated agreement on the mechanical properties of sliceable English

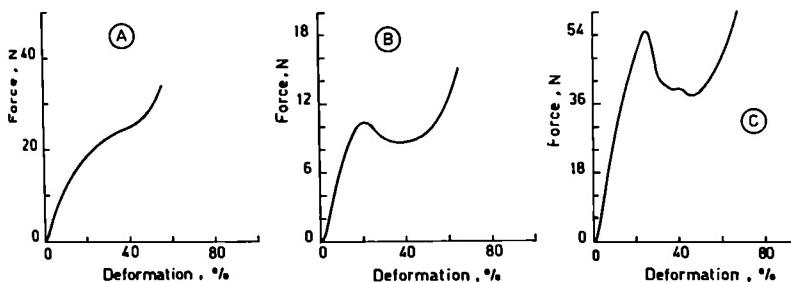


Fig. 5. Typical force-deformation curves for: (A) Silano cheese; (B) spreadable English cheese; (C) sliceable English cheese.

cheese has confirmed the equivalence of the measurements in all the participant laboratories.

4. RECOMMENDATIONS FOR MEASUREMENT PROCEDURES

4.1. Introduction

The difference between the results produced by the different laboratories that emerged, and the analysis of the factors which determined them, have indicated what contextual factors should be controlled and what information should accompany mechanical property data. Many of these factors were taken into account in designing the collaborative experiment while others arose in the course of the programme itself. The recommended information is detailed in Table 5, Chapter 30, by McKenna.

Next, the influence of some of these factors on mechanical properties of cheeses as reported in the literature will be briefly reviewed. In addition, measurement conditions will be analysed on the basis of physical considerations and limitations of commonly available test equipment. Finally, a suggested basis for comparing such cheese results will be outlined.

4.2. Shape

Prismatic samples exhibit force-compression behaviour which is different from that exhibited by cylindrical samples having the same height and the same cross-sectional area (Brington and Bourne, 1972). This is due to the differences in the stress distribution within the sample (Hammerle and McClure, 1971).

For mechanical tests, cylindrical specimens give simpler stress distributions within the sample than prisms (Hammerle and McClure, 1971). Cylindrical specimens are more convenient than prismatic samples because of the symmetrical distribution of stress in each cross-section. However, the sample preparation presents some difficulties. In fact, cheese samples prepared by means of a 'cork-borer' usually have a conical shape. To avoid that, it is necessary to keep the rate of penetration of the cork-borer into the bulk cheese uniform and this can be done only by using a mechanically-driven device.

In some cases it is more convenient to use prismatic samples which can be easily prepared either by means of a mitre box and a sharp knife or by means of a device like that shown in Fig. 6 which consists of a network of metallic cutting wires of adjustable spacing.

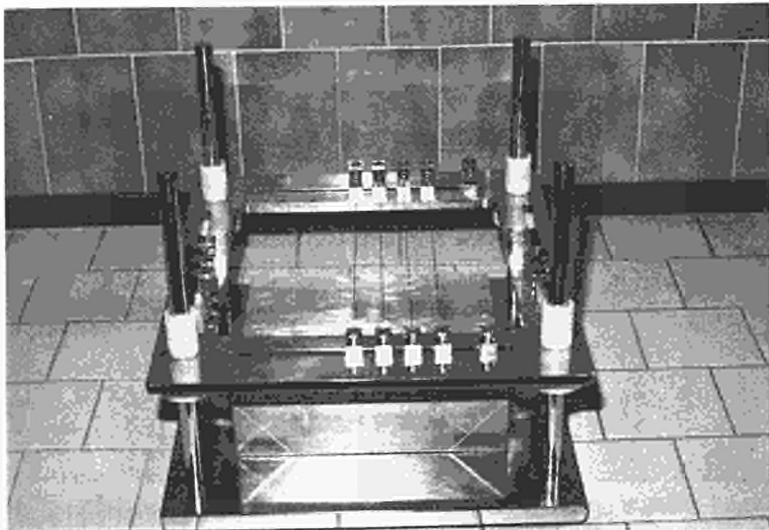


Fig. 6. Metal wire cheese-cutting device for preparation of prismatic samples (courtesy of Dr M. Lucisano, Department of Food Science and Technology and Microbiology, University of Milan).

This is so for flaky and brittle cheeses which often break during penetration by the cork-borer or when the core is extracted.

4.3. Size

During compression part of the applied force is used to overcome friction between the upper and lower flat surfaces of the sample and the metal platens of the test instrument. In addition, forces acting on these surfaces cause the vertical surfaces close to the platens to deform more slowly than the central region so that a barrel shape is produced (Fig. 7). Consequently, the mechanical response of the sample will change with variation in sample dimensions (von Sachs, 1924; Brington and Bourne, 1972). (See also Chapter 29 by Bagley.)

Figure 8 shows the effect of variation of the length/diameter ratio of samples of a pasta filata cheese (Silano) on the apparent modulus of elasticity. The ratio must be >1 if the results are to be independent of it. Similar results have been found for prismatic specimens (Masi and Acierno, 1986).

In compression tests, the stress measured contains both the stress

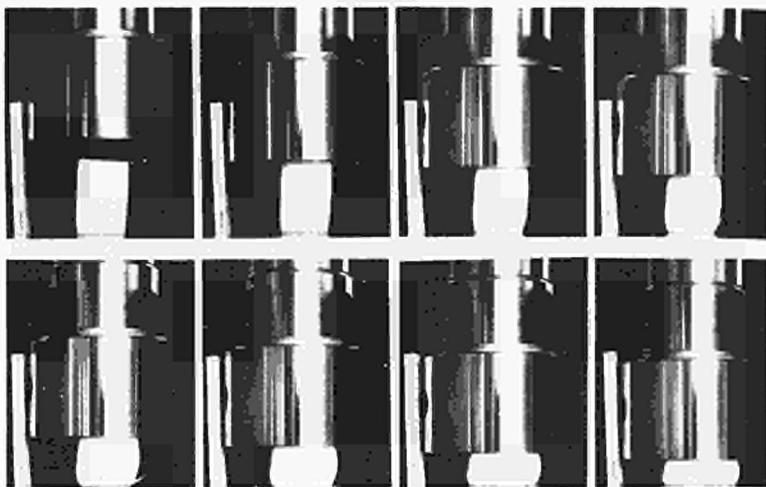


Fig. 7. Typical cheese sample deformation during a compression test.

required to deform the cheese structure and the friction between the sample and the metal platens. Increasing the sample contact area increases the friction and consequently the sample appears more rigid.

The effect of restricting expansion of the sample decreases with the sample height; the taller the sample, the smaller the influence on the measured mechanical properties becomes.

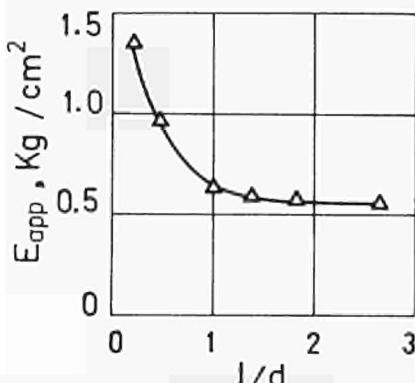


Fig. 8. Apparent modulus of elasticity of Silano cheese as a function of specimen aspect ratio l/d .

Sample dimensions should be so selected as to minimise their influence on the measured mechanical properties. In this context it is interesting to note that with increasing sample aspect ratio, i.e. length-to-diameter ratio, the mechanical properties become almost independent of sample size (Masi and Acierno, 1986).

4.4. Compression Rate

Cheeses are viscoelastic and thus their rheological behaviour depends on the strain history, e.g. force-compression data vary with the rate at which the sample is deformed (Voisey, 1975; Sherman and Deghaidy, 1978).

Table 7 summarises the effect of strain rate on some mechanical properties of several Italian cheeses. The cheeses listed have been chosen so as to cover a wide range of textural attributes. Pecorino Romano and Parmigiano Reggiano are strong and crumbly; Provolone, Montasio and Caciotta, which were tested at an early stage of ripening, have a waxy body with a slightly wood-like texture; while Taleggio, Fontina and Bel Paese cut cleanly and are spreadable at room temperature.

During loading some stress relaxation occurs through breakage and reformation of labile bonds within the casein network (Masi and Addeo,

TABLE 7
TYPICAL MECHANICAL PROPERTIES OF ITALIAN CHEESES AT 20°C

Cheese	Cross-head speed (mm min ⁻¹)	σ_y (N m ⁻² (10 ⁵))	ε_y (%)	E_{app} (N m ⁻² (10 ⁵))	W (N m ⁻² (10 ⁴))
Parmigiano Reggiano	5	1.29	13	19.8	1.12
	50	2.45	11	35.8	1.85
Pecorino Romano	5	2.40	22	28.4	3.40
	50	3.23	20	33.6	5.09
Caciotta Sarda	50	0.72	25	6.2	1.13
	200	0.93	28	5.7	1.73
Provolone	50	0.97	41	2.4	1.89
	200	1.40	44	3.6	2.97
Montasio	50	2.28	45	4.7	8.96
	200	2.90	55	4.5	7.52
Bel Paese ^a	50	1.40	—	0.67	2.69
	200	1.60	—	0.60	2.83
Fontina ^a	50	1.18	—	0.34	1.56
	200	1.12	—	0.45	2.04
Taleggio ^a	50	0.04	—	0.50	0.95
	200	0.05	—	0.61	1.25

^aCheeses which do not show a rupture or yield point.

1986). With increasing strain rate, the number of bonds which have sufficient time to break and reform decreases and thus the cheese will appear more rigid.

In selecting the appropriate cross-head speed, the following should be considered:

- (a) The cross-head speed should not be very low so that the effect of relaxation processes which take place during the sample loading is minimised.
- (b) Cross-head speed should be at least 3–4 times slower than the strip-chart speed if collection of data is not electronic.
- (c) Cross-head speed should be considerably slower than the response rate of the data collection instruments.

When using a potentiometric-type strip-chart recorder, as is normally supplied for force-deformation-type machines (e.g. Instron), the deformation rate must be less than 20 cm min^{-1} .

The selection of the deformation rate is somewhat arbitrary and is often based on the need to obtain good force-deformation diagrams. With many cheeses this is obtained with a cross-head speed of 5 cm min^{-1} .

Mechanical properties are often correlated with textural properties. This suggests that mechanical properties should be measured at deformation rates comparable to chewing rate, i.e. 150 cm min^{-1} (Bourne, 1974). Such rates are not available on current popular test machines. It is therefore necessary to measure mechanical properties at different deformation speeds. For example, it is convenient to measure mechanical properties at deformation rates of 5 cm min^{-1} and at least at two others in the range 0 – 20 cm min^{-1} . In this way, if a test at high deformation rate cannot be performed, the approximate behaviour at high deformation rate can be predicted by extrapolation of the data at low deformation rate. In this case, however, caution should be exercised when drawing conclusions on the failure mode since the way in which the sample fails depends greatly on the particular manner and rate of application of force.

4.5. Boundaries

In characterising by compression tests such soft and sticky materials as cheeses, the problem of friction between sample and compression platens cannot be neglected. On one hand, lubrication appears to be effective in obtaining reproducible results which are independent of the sample geometry (Bagley *et al.*, 1986; also Chapter 29 by Bagley) and agree with results from other testing modes. On the other hand, lubrication introduces

complications due to the influence of the rheological properties of the lubricating layer. This problem can be obviated by bonding the sample to the platens, as is often done when examining rubber systems (Gent and Lindley, 1959). It has been shown that by applying shape corrections to the nominal stress during deformation, agreement between stress-strain behaviour of lubricated and bonded samples can be achieved, at least over the initial range of strain. This correction, if no volume change occurs, is done in the case of lubricated samples by multiplying the apparent stress by the ratio between the actual sample height, $h(t)$, and the undeformed sample dimension, $h(0)$, while for bonded samples the following relationship is applied:

$$\sigma_{BC} = \sigma_B \left/ \left(1 + \frac{R_0^2}{2h^2} \right) \right. \quad (1)$$

where σ_{BC} is the corrected bonded stress, σ_B is the nominal stress in bonded compression, and R_0 and h are the radius of the undeformed sample and its actual height, respectively.

The results of these collaborative experiments have confirmed that reproducible mechanical property data can be obtained by using constant friction conditions between the sample and the platens. Additionally, to obtain meaningful compression data for cheese, it is suggested that compression tests be carried out both under bonded and lubricated conditions so as to characterise the limiting behaviour under all possible frictional conditions between the platens and the sample (Fig. 9).

4.6. Force–Displacement Curve Analysis

Experimental results should preferably be in the form of a force-displacement curve. In addition, some derived quantities such as yield stress and strain, elastic modulus and work up to a given characteristic point should be quoted.

In accordance with engineering convention, stress and strain at any point may be evaluated in terms of the cross-sectional area and the length of the undeformed sample. However, in adopting this approximation one should be aware of the fact that by using undeformed dimensions in place of the actual dimensions, significant differences between apparent and true properties exist in the case of large deformation experiments. In characterising soft cheeses, the shape changes occurring during the deformation should be taken into account.

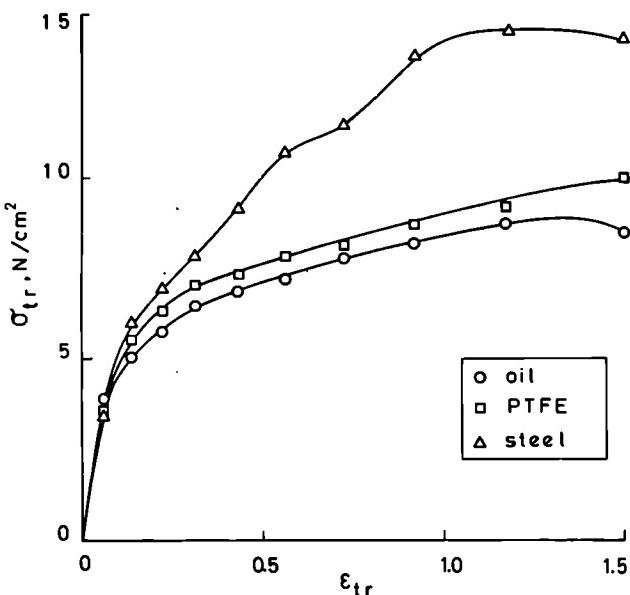


Fig. 9. Stress-strain behaviour of Silano cheese using three different friction conditions between sample and platens.

Figure 10 shows typical force-deformation curves for cheeses. All the curves show an inflexion point very close to the origin. The shape of the force-deformation curve suggests that solid cheeses may be grouped into two categories: those which exhibit a rupture or yield point, and those which do not.

The apparent modulus of elasticity should be calculated from the slope of the first clearly linear part which follows any initial non-linear part of the force-deformation diagram or, where no such clearly linear part exists, from the slope of the linearised middle third of the diagram.

For cheeses whose force-deformation diagram shows a rupture or yield point, the stress and strain evaluated at the rupture (or yield) point together with the rupture (or yield) work per unit volume should be quoted. Beyond the point of fracture, reproducibility cannot be expected and equations for stress and strain are no longer valid.

For cheeses whose force-deformation diagram does not show any rupture or yield point, stress and work per unit volume should be evaluated at a large deformation, for example at 80%.

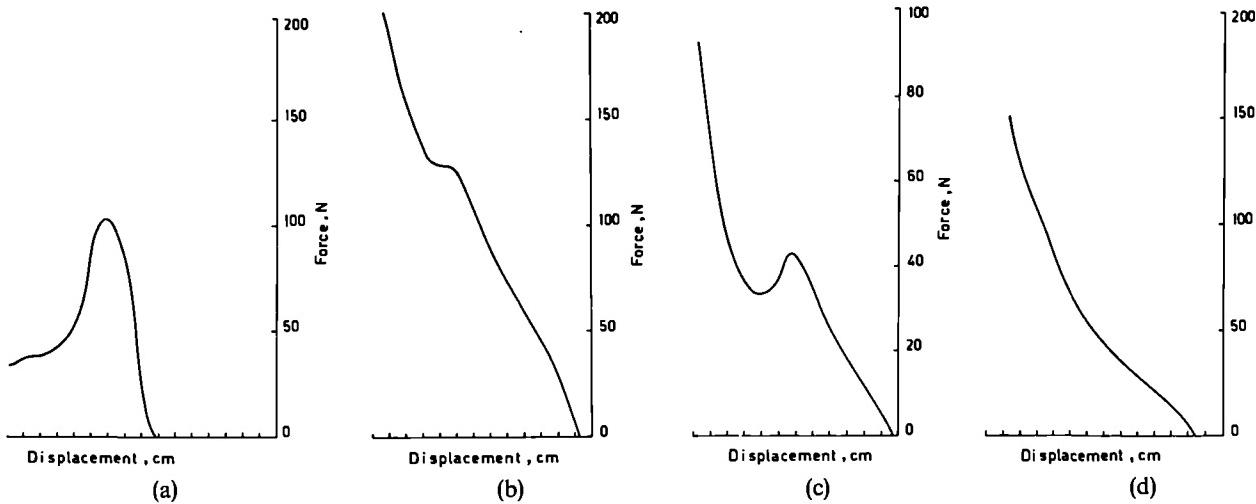


Fig. 10. Force-displacement curves for various cheeses: (a) Parmigiano Reggiano; (b) Montasio; (c) Provolone; (d) Bel Paese
(displacement increasing from right to left in each example).

5. SUGGESTED BASIS FOR COMPARING CHEESE RESULTS

5.1. Measurement Conditions

Shape	Vertical cylinder or prism.
Size	Aspect ratio > 1 (i.e. $\frac{\text{sample height}}{\text{sample width or diameter}} > 1$).
Cross-head speed	5 cm min ⁻¹ and two other speeds in the range 0–20 cm min ⁻¹ .
Boundaries	Both bonded and lubricated platens.

5.2. Results Data to be Reported

- (a) Rupture (or yield) stress.
- (b) Rupture (or yield) strain.
- (c) Elastic modulus.
- (d) Rupture (or yield) work per unit of volume.
- (e) Failure mode.

If the cheese does not exhibit rupture or yield, then the stress and the work per unit of volume corresponding to 80% deformation should be quoted.

5.3. Final Remarks

Before concluding, it is worth pointing out that these recommendations were made without consideration of the reason for collecting mechanical property information as, for example, for correlation with sensory properties or for quality and process control. Frequently, these applications require special test conditions in order to show structural differences among the samples. The specification of appropriate measurement conditions cannot be made on a general basis but should be related to case by case. The purpose of the work reported here was essentially to verify the possibility of obtaining reproducible mechanical data on cheeses in different laboratories and to select the measurement conditions which facilitate the generation of such reproducible data. From this point of view it can be said that such concerted action has succeeded.

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Mechanical Properties Subgroup Chairman, Professor Brian McKenna, for their able leadership and guidance in the past years. Thanks are also due to the participating laboratories and to the members of the Mechanical Properties Subgroup, without whose help this work could not have been achieved. In particular, to Dr Green and the late Dr E. W. Evans of the Food Research Institute, Reading, for their advice and useful comments.

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DISCUSSION

M. A. Roques noted how important not only testing condition uniformity was but also uniformity of *sampling*, as between the different laboratories. *P. Masi*, agreeing, said that Italian cheeses presented no difficulty in this respect but ripened cheeses, for example, and the English cheeses, showed more non-uniformity throughout the cheese, so sampling procedure was very important.

Mechanical Properties of Apples: I. Results of the Collaborative Study

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SUMMARY

Quasi-static compression tests and stress-relaxation tests were carried out on apples of the variety 'Golden Delicious'. As biological change during distribution is a major constraint on collaborative work in this area, no common reference material could be used and locally-purchased samples of similar products were used.

1. INTRODUCTION

Eight laboratories in seven countries collaborated. They are listed in Table 1.

The purpose of this study was:

- to collect data on the mechanical properties of Golden Delicious apples;
- to ascertain the effect of apple origin on the variability of such data for this variety;
- to determine the relationship between properties obtained from compression tests up to failure and properties obtained from relaxation tests (as suggested by Jacinto *et al.*, 1984).

Test specifications were drawn up by the authors (De Baerdemaeker and Tijskens) and are described in the next three sections.

TABLE 1
PARTICIPATING LABORATORIES

<i>Country</i>	<i>Code</i>	<i>Laboratory</i>
The Netherlands	CPRE	Centre for Poultry Research and Extension 'Het Spelderholt', Beekbergen
France	ENSIA	Ecole Nationale Supérieure des Industries Agricoles et Alimentaires
UK	FRIN	Food Research Institute, Norwich
Belgium	KUL	Catholic University, Leuven
Spain	PUM	Polytechnic University of Madrid
The Netherlands	SI	Sprenger Institute
Denmark	TUD	Technical University of Denmark
Italy	UN	University of Naples

2. THE MATERIAL

The widespread apple variety 'Golden Delicious' was chosen as the test material. As much as possible of the following data on the apple history were gathered for the locally-purchased apples: fruit origin, picking date, storage conditions, testing date and ambient temperature and relative humidity (see Table 2).

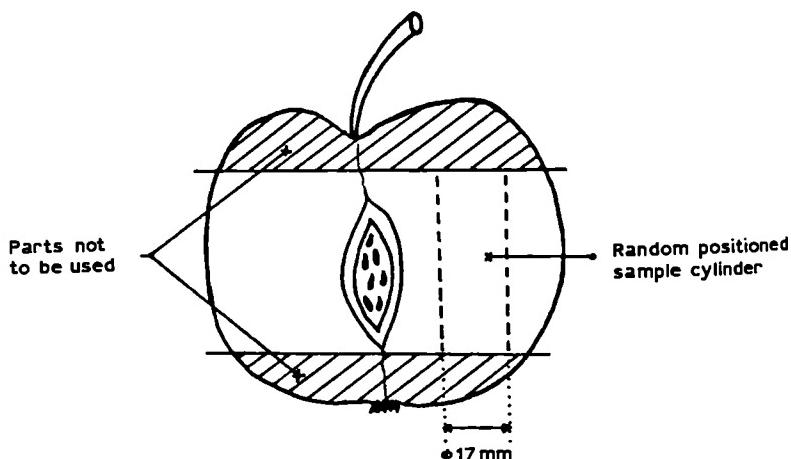


Fig. 1. Location of apple cylinders for testing.

TABLE 2
HISTORY OF APPLES USED IN THE COLLABORATIVE TESTS: VARIETY 'GOLDEN DELICIOUS'

Laboratory	Origin of fruit	Picking date (1984)	Storage conditions	Test date (1984)	Ambient temp (°C)	Relative humidity
CPRE ENSIA	— Val de Loire	— 13/12	7°C 4°C in closed plastic bags	30/11–10/12 18/12	— 18	— —
FRIN	Cotton Norwich	22/10	5°C in trays covered with Polyethylene sheets	7/11	22	—
KUL PUM	— Experimental farm— PUM	— 6/10	4°C 12°C–20°C	10/10 19/10	20 17	— —
SI TUD	— —	25/10 11/10	4°C and 80% RH 4°C	22/11 23/10, 5/12 and 6/12 2/11	21–22 18·6	— —
UN	—	—	4°C for 1 week	—	—	—

3. PREPARATION OF SAMPLES

Before testing, the apples were acclimatised for several hours at room temperature. They were then selected at random from the sample batch and labelled. The apples were cut as shown in Fig. 1 and the central part used for tests. A corkborer (internal diameter 17 mm) was used to cut a cylinder of apple flesh from a random position around, but not including the apple core. This cylinder was then pushed out from the corkborer until it protruded 1–2 mm and was then cut flush to the corkborer using a razor blade. It was pushed out a further 17 mm and again cut flush with the corkborer. In an identical manner a 9 mm sample was also obtained from the same cylinder. This gave two samples for testing per cylinder of apple flesh. The remainder of the apple cylinder was discarded.

4. MEASUREMENT PROCEDURE

All measurements were made at room temperature with the testing machines in compression mode. The upper and lower compression platens were of polished stainless steel and of much greater diameter than the apple samples. No lubrication was used at the platen–apple contact surface and, after each sample had been tested, the platen surfaces were wiped dry.

Cross-head speed was kept constant at 20 mm min⁻¹ for all measurements. All results were recorded in the form of recorder charts supplemented in some cases by electronic data recording.

4.1 Quasi-static Compression Tests

From the recorded force–deformation curves and using the original sample dimensions, a stress–strain curve could be obtained from which the following mechanical properties were derived:

1. Apparent elastic modulus, E_{app} (N m⁻²) defined in this study as the slope of the middle third part (between 1/3 and 2/3 of the failure stress value) of the stress–strain curve.
2. Failure stress, σ_f (N m⁻²).
3. Failure strain, ϵ_f .
4. Failure energy density, W_f (J m⁻³)
i.e. the area under the stress–strain curve up to failure.

Figure 2 shows a representation of a stress–strain curve and how the above mentioned properties are obtained from it. In these tests two sample heights (17 mm and 9 mm) were used.

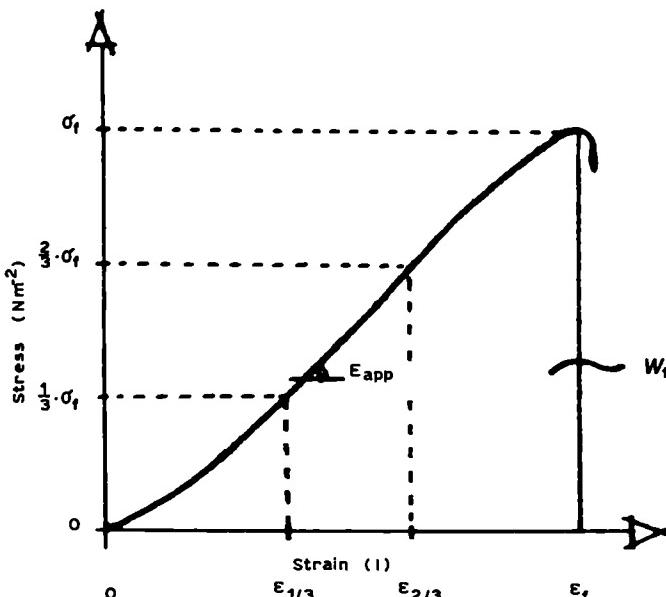


Fig. 2. Stress-strain curve and derived mechanical properties.

4.2 Relaxation Test

The test involved the determination of the initial slope of the force relaxation curve. The samples, of height 17 mm, were compressed with a speed of 20 mm min^{-1} up to a specified maximum compressive force (50 N in most cases). At that point the cross-head was stopped and the force monitored as a function of time.

To characterise the viscoelastic behaviour of the apple flesh a weighted mean relaxation rate (WMRR) was calculated from the measured slope and the maximum initial compressive force. As the apple flesh exhibits more viscous behaviour the value of this weighted mean relaxation rate increases. The calculation formula is based on the following. For any viscoelastic material the stress relaxation may be written as

$$\sigma(t) = \varepsilon_0 \sum_0^n E_i e^{-t/T_i} \quad (1)$$

where $\sigma(t)$ = stress at time t after start of relaxation; ε_0 = strain at start of relaxation; E_i = elastic modulus of i th term of relaxation model; T_i = time

constant of i th term of relaxation model. At time $t = 0$ the value of this stress is

$$\sigma(0) = \varepsilon_0 \sum_0^n E_i \quad (2)$$

from which the initial strain is

$$\varepsilon_0 = \frac{\sigma(0)}{\sum_0^n E_i} \quad (3)$$

Taking the first time-derivative of eqn. (1) at time $t = 0$ gives

$$\left. \frac{d\sigma(t)}{dt} \right|_{t=0} = \varepsilon_0 \sum_0^n E_i \frac{-1}{T_i} e^{-t/T_i} \Big|_{t=0} = \varepsilon_0 \sum_0^n -\frac{E_i}{T_i} \quad (4)$$

Substituting eqn. (3) into eqn. (4) and rearranging yields

$$\frac{-\frac{d\sigma(t)}{dt}}{\sigma(0)} \Big|_{t=0} = \frac{\sum_0^n E_i (1/T_i)}{\sum_0^n E_i} \quad (5)$$

This last equation (5) is the expression for the weighted mean relaxation rate (WMRR), in which the elastic moduli E_i are the weighting factors. Since $F(t) = \sigma(t)A$, where A is the sample cross section, it can also be calculated as

$$\text{WMRR} = \frac{-\frac{dF(t)}{dt}}{F(0)} \Big|_{t=0} = \frac{\sum_0^n E_i (1/T_i)}{\sum_0^n E_i} \quad (6)$$

The inverse of the weighted mean relaxation rate was also calculated and is referred to as the weighted mean relaxation time (WMRT)

$$\text{WMRT} = 1/\text{WMRR} \quad (7)$$

Because of the difficulty in relaxation studies of finding the true instantaneous initial slope ($dF(t)/dt$ at $t = 0$), it was replaced by the slope of the least-squares fit regression line through the three points of the curve at 1 s, 3 s and 5 s after the cross-head is halted. This slope has a negative value and is expressed in N s^{-1} . This procedure is shown in Fig. 3.

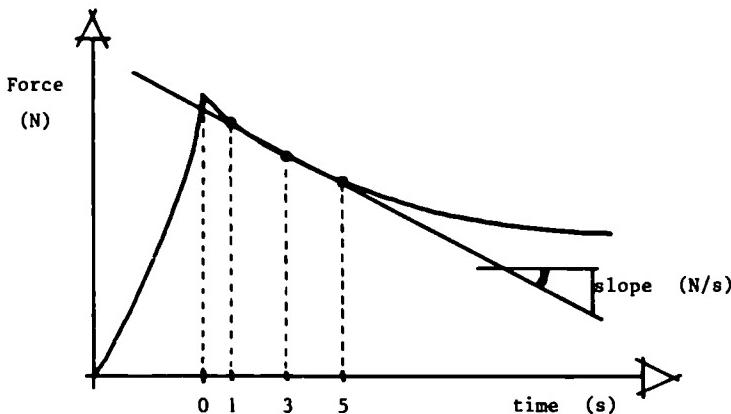


Fig. 3. Determination of the slope of the relaxation curve.

5. STATISTICAL TREATMENT OF THE RESULTS

The results obtained by the participants were first screened and then processed to determine the descriptive statistics and analysis of variances (SAS Institute, 1982a,b).

In detail, the statistical treatment involved the following steps:

1. Identification and elimination of outliers within each individual experimental data set.
2. Calculation of the mean value (MEAN), standard deviation (STD) and coefficient of variation (CV) within each individual experimental data set with outliers discarded.
3. Analysis of variances and Duncan grouping of the individual variables over all data sets.
4. Linear regression to establish the relationship between the mechanical properties from compression tests and those from relaxation tests.

Regarding step (1), in which the original data were considered, outliers were identified by performing a *t*-test at an $\alpha = 0.05$ level. Table 3 shows the number of observations before and after outlier elimination for each measured variable in each group.

The descriptive statistics for the mechanical properties within each group are given in Table 4. For all participating laboratories the coefficients of

TABLE 3
NUMBER OF OBSERVATIONS BEFORE AND AFTER OUTLIER ELIMINATION

Lab.	Sample height	Apparent elastic modulus		Failure stress		Failure strain		Failure energy density		Weighted mean relaxation rate	
		N	N*	N	N*	N	N*	N	N*	N	N*
CPRE	9	30	28	30	28	30	28	30	28	—	—
CPRE	17	30	29	30	29	30	29	30	26	25	21
ENSIA	9	30	25	30	26	30	27	30	28	—	—
ENSIA	17	30	27	30	28	30	29	30	27	30	26
FRIN	9	10	10	10	10	10	10	10	10	—	—
FRIN	17	10	10	10	9	10	10	10	9	10	9
KUL	9	24	20	25	22	25	25	25	22	—	—
KUL	17	26	23	26	23	26	22	26	22	33	32
PUM	9	10	10	10	10	10	10	10	10	—	—
PUM	17	10	10	10	10	10	9	10	9	9	8
SI	9	30	28	30	28	30	27	30	27	—	—
SI	17	30	26	30	25	30	27	30	26	10	9
TUD	9	55	49	52	47	51	46	51	49	—	—
TUD	17	50	47	50	47	50	45	49	46	30	24
UN	9	—	—	—	—	—	—	—	—	—	—
UN	17	—	—	—	—	—	—	—	—	10	10

N = number of observations in original data set.

N* = number of observations after outlier elimination.

variation for relaxation tests tend to be smaller than those for compression tests. There is no obvious explanation for this.

An analysis of variance was made to see whether the apple history (origin, age, state, conditioning, ...) and/or sample height had a significant influence on the mechanical properties of the apples. Table 5 shows the results of this procedure with significance test at the $\alpha = 0.05$ level. The results demonstrate marked differences due to the history of the apples used.

In the Duncan grouping of the individual means shown in Table 6, means with the same letter are not significantly different at the $\alpha = 0.05$ level.

A supplementary result emerged from a separate analysis of variances on data submitted by two of the participating laboratories (PUM, UN) from compression tests at different compression speeds (10, 20 and 50 mm min⁻¹). The analysis showed that the differences caused by testing at

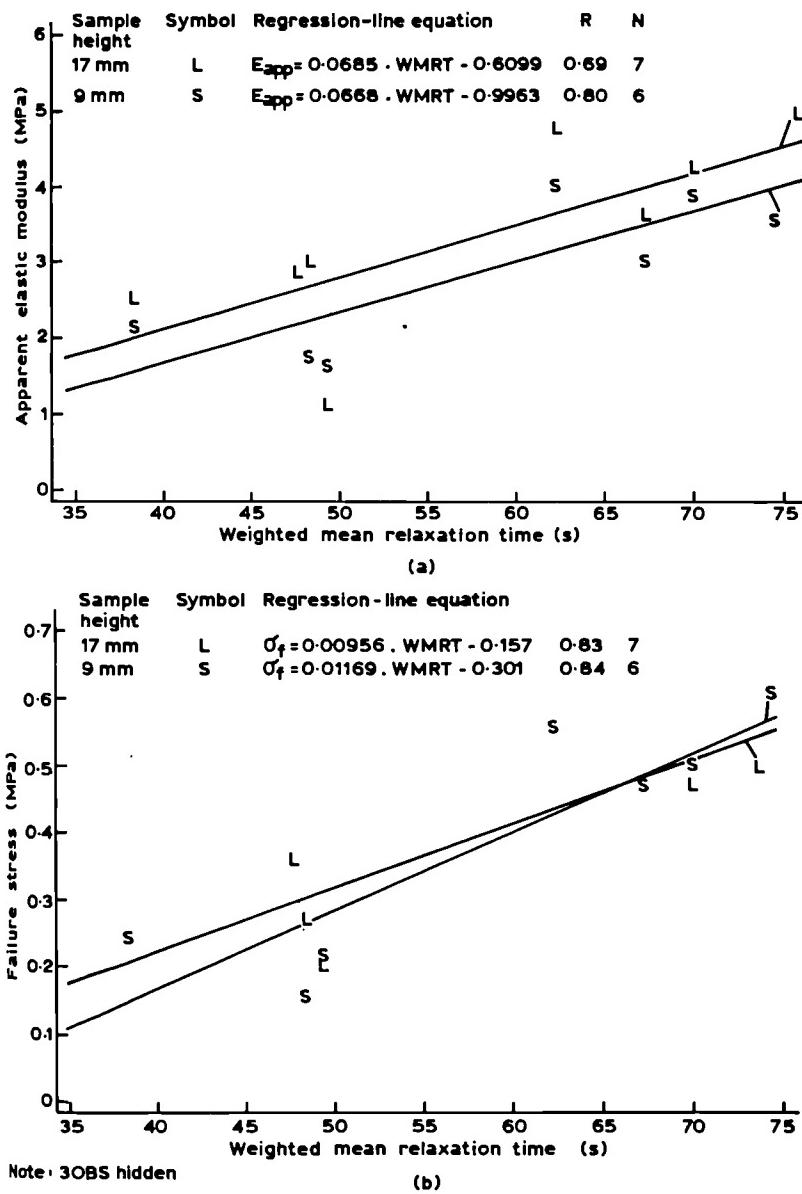


Fig. 4. (a) Relationship between apparent elastic modulus and weighted mean relaxation time. (b) Relationship between failure stress and weighted mean relaxation time.

TABLE 4
DESCRIPTIVE STATISTICS FOR THE MECHANICAL PROPERTIES

(a) Compression tests

<i>Laboratory</i>	<i>CPRE</i>	<i>EN SIA</i>	<i>FRIN</i>	<i>KUL</i>	<i>PUM</i>	<i>SI</i>	<i>TUD</i>	<i>UN</i>
Apparent elastic modulus E_{app} (MPa)								
<i>h</i> = 9 mm	MEAN	1.811	1.604	3.055	3.884	9.277	2.159	3.967
	STD	0.409	0.212	0.258	0.663	1.857	0.437	0.579
	CV	0.226	0.132	0.085	0.171	0.200	0.203	0.146
<i>h</i> = 17 mm	MEAN	2.993	1.118	3.607	4.191	2.841	2.549	4.732
	STD	0.206	0.163	0.502	0.474	0.528	0.228	0.663
	CV	0.069	0.146	0.139	0.113	0.186	0.090	0.140
Failure stress σ_f (MPa)								
<i>h</i> = 9 mm	MEAN	0.153	0.207	0.470	0.496	1.329	0.239	0.561
	STD	0.073	0.026	0.042	0.036	0.238	0.048	0.032
	CV	0.478	0.126	0.090	0.074	0.180	0.202	0.059
<i>h</i> = 17 mm	MEAN	0.276	0.193	0.469	0.478	0.359	0.241	0.554
	STD	0.034	0.024	0.033	0.031	0.081	0.015	0.042
	CV	0.126	0.125	0.071	0.066	0.228	0.062	0.076
Failure strain ε_f (l)								
<i>h</i> = 9 mm	MEAN	0.165	0.197	0.144	0.207	0.228	0.138	0.364
	STD	0.021	0.016	0.012	0.106	0.027	0.023	0.055
	CV	0.129	0.082	0.083	0.514	0.122	0.169	0.153
<i>h</i> = 17 mm	MEAN	0.123	0.138	0.127	0.131	0.174	0.115	0.288
	STD	0.009	0.014	0.012	0.040	0.016	0.012	0.056
	CV	0.080	0.104	0.100	0.308	0.095	0.105	0.197

Failure energy density W_f (kJ m^{-3})

$h = 9 \text{ mm}$	MEAN	12.7	16.3	18.5	27.9	123.4	16.8	128.4
	STD	2.38	2.39	2.37	18.17	37.95	2.36	29.90
	CV	0.187	0.147	0.128	0.649	0.307	0.140	0.233
$h = 17 \text{ mm}$	MEAN	15.3	11.1	28.8	35.6	25.3	16.7	101.6
	STD	1.81	1.63	2.70	16.98	7.16	2.58	21.58
	CV	0.118	0.146	0.094	0.476	0.282	0.155	0.212

(b) Relaxation tests

Laboratory	CPRE	ENSAIA	FRIN	KUL	PUM	SI	TUD	UN	
Weighted mean relaxation rate WMRR (litre/second)									
$h = 17 \text{ mm}$	MEAN	0.0206	0.0202	0.0149	0.0144	0.0210	0.0262	0.0161	0.0617
	STD	0.0009	0.0013	0.0011	0.0014	0.0012	0.0021	0.0013	0.0061
	CV	0.047	0.064	0.077	0.096	0.059	0.080	0.079	0.100
Weighted mean relaxation time WMRT (second)									
$h = 17 \text{ mm}$	MEAN	48.48	49.45	67.40	70.13	47.73	38.32	62.35	16.35
	STD	2.195	3.164	5.085	7.724	2.750	2.953	4.963	1.718
	CV	0.045	0.064	0.075	0.110	0.058	0.077	0.080	0.105

TABLE 5
RESULTS FROM THE ANALYSIS OF VARIANCES

Mechanical property	Factor influences					
	Apple history (Lab)			Sample height		
	F value	prob (>F)	sign 5%	F value	prob (>F)	sign 5%
Apparent elastic modulus	91.37	0.0001	yes	0.72	0.3972	no
Failure stress	116.0	0.0001	yes	8.81	0.0032	yes
Failure strain	171.4	0.0001	yes	126.5	0.0001	yes
Failure energy density	249.4	0.0001	yes	27.46	0.0001	yes
Weighted mean relaxation rate	642.2	0.0001	yes	—	—	—
Weighted mean relaxation time	176.8	0.0001	yes	—	—	—

TABLE 6
DUNCAN GROUPING OF THE INFLUENCING FACTORS
(Groups with the same letter are not significantly different at the $\alpha = 0.05$ level)

Apparent elastic modulus (MPa)							
Duncan grouping	Lab.	Mean	N	Duncan grouping	Sample height	Mean	N
A	PUM	6.059	20	A	17	3.294	172
	TUD	4.342	96		9	3.216	170
	KUL	4.048	43				
C	FRIN	3.331	20				
	CPRE	2.412	57				
	SI	2.347	54				
E	ENSIA	1.352	52				
Failure stress (MPa)							
Duncan grouping	Lab.	Mean	N	Duncan grouping	Sample height	Mean	N
A	PUM	0.844	20	A	9	0.419	171
	TUD	0.558	94		17	0.376	171
	KUL	0.487	45				
C	FRIN	0.469	19				
	SI	0.240	53				
	CPRE	0.215	57				
D	ENSIA	0.200	54				

TABLE 6—*continued*

<i>Failure strain (l)</i>							
<i>Duncan grouping</i>	<i>Lab.</i>	<i>Mean</i>	<i>N</i>	<i>Duncan grouping</i>	<i>Sample height</i>	<i>Mean</i>	<i>N</i>
A	TUD	0.326	91	A	9	0.227	173
B	PUM	0.202	19	B	17	0.172	171
C	KUL	0.171	47				
C	ENSIA	0.167	56				
D	CPRE	0.144	57				
D	FRIN	0.135	20				
D	SI	0.127	54				

<i>Failure energy density (kJ m⁻³)</i>							
<i>Duncan grouping</i>	<i>Lab.</i>	<i>Mean</i>	<i>N</i>	<i>Duncan grouping</i>	<i>Sample height</i>	<i>Mean</i>	<i>N</i>
A	TUD	115.4	95	A	9	55.1	174
B	PUM	76.9	19	B	17	42.9	165
C	KUL	31.8	44				
C	FRIN	23.4	19				
D	SI	16.8	53				
D	CPRE	14.0	54				
D	ENSIA	13.81	55				

<i>Weighted mean relaxation rate (litre/second)</i>				<i>Weighted mean relaxation time (second)</i>			
<i>Duncan grouping</i>	<i>Lab.</i>	<i>Mean</i>	<i>N</i>	<i>Duncan grouping</i>	<i>Lab.</i>	<i>Mean</i>	<i>N</i>
A	UN	0.0617	10	A	KUL	70.13	32
B	SI	0.0262	9	A	FRIN	67.40	9
C	PUM	0.0210	8	B	TUD	62.35	24
C	CPRE	0.0206	21	C	ENSIA	49.45	26
C	ENSIA	0.0202	26	C	CPRE	48.48	21
D	TUD	0.0161	24	C	PUM	47.73	8
D	FRIN	0.0149	9	D	SI	38.32	9
E	KUL	0.0144	32	E	UN	16.35	10

different compression speeds are significant at the $\alpha = 0.01$ level for all the mechanical properties considered.

From the graphical representation of the data given in Table 4 shown in Fig. 4 it can be seen that there is a fairly linear relationship between the weighted mean relaxation time derived from relaxation tests and the apparent elastic modulus and failure stress derived from quasi-static compression tests. This might suggest that a relaxation test could provide enough information on the firmness (failure strength, apparent elastic modulus) of apples.

Figure 4 also shows the regression lines and the corresponding correlation coefficients. A refined algorithm for the determination of the initial slope which can be implemented easily in all the cooperating laboratories would perhaps improve this relationship.

6. CONCLUSIONS

Fruit of the same variety and harvested around the same time, but originating from different countries, exhibit large differences in mechanical properties. This fact can be used to establish cooperative research where properties are intended to be different. Congruences of experimental data from the different laboratories show that the measurement procedure gave consistent results. The relaxation data can be used as an alternative test to estimate failure strength and possibly bruise-susceptibility of apples. Care should be taken to write test specifications so that they can be executed on the various makes of equipment in the different laboratories.

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Mechanical Properties of Apples: II. Dynamic Measurement Methods and Their Use in Fruit Quality Evaluation

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SUMMARY

Fruit firmness is an important criterion in determining the quality of apples. Both producer and consumer acceptance may be highly dependent on this property.

Dynamic methods, both destructive and non-destructive, of evaluating the fruit firmness are compared together and with a static method.

The results of tests on Golden Delicious apples are presented and the suitability of each method evaluated.

1. INTRODUCTION

Fruit quality is a concept based on several criteria which depend on the objective. Firmness is an important factor to take into account since most, if not all, fruits exhibit a substantial change in firmness during the process of ripening. Because the ripening process itself varies from fruit to fruit, a large variation in firmness may be found among individual fruits in the same containers or harvested at the same time. This difference in appearance may considerably influence the consumer acceptance of the product as it is related to the 'eating maturity' and the fruit texture.

From the producer's point of view, firmness can be an indication of the shelf life of the product.

2. DYNAMIC MEASUREMENTS

Dynamic testing concerns the time-varying mechanical response of a certain material to a time-varying mechanical excitation. This excitation may be either a force or a displacement at some point of the system under study and can be instantaneous (impact analysis), periodic (harmonic analysis) or random.

The most direct way of describing the system response is simply to express the instantaneous value of the displacement, velocity or acceleration of a given measuring point as a function of time, either numerically or analytically by means of some mathematical expression.

Although this is sometimes sufficient, in most cases more sophisticated methods are used to describe the vibratory motion. From an analysis of the system response in the frequency domain, dynamic properties are obtained. Resonant frequencies, stiffness and damping are examples of such properties.

Considerable efforts have already been made to determine those mechanical properties which are related to the quality criteria on which consumer acceptance is based (Diehl and Hamann, 1979; Tijskens, 1979). From quasi-static compression tests, the normal stress to failure was found to give useful information about the internal quality of apples at the time they lose their consumer acceptability. Nevertheless, static tests alone are not sufficient for the quality evaluation of hard fruits.

2.1. Destructive Dynamic Testing

Destructive dynamic tests on a cylindrical specimen also reveal some mechanical characteristics of the fruit. In the analysis the specimen is considered as a spring-damper-mass system. Measured resonant frequencies can then be used to calculate the moduli of elasticity and associated loss moduli, which are a measure of internal damping.

For a direct measurement of the elastic modulus of the apple flesh the following method is used. A cylindrical sample of apple tissue of mass M_s , loaded with a mass M , is placed on a force transducer which is mounted on a vibration exciter. The exciter is driven by a pseudo-random noise signal with a frequency bandwidth of 0–400 Hz. A low-mass accelerometer is placed on top of the system on the same axis as the load cell (Fig. 1). This system corresponds to the spring-damper-mass system shown in Fig. 2. This configuration contains a spring with spring constant k , a damper with damping constant c and a mass m equal to $M + M_s/3$ since the sample mass cannot be completely ignored.

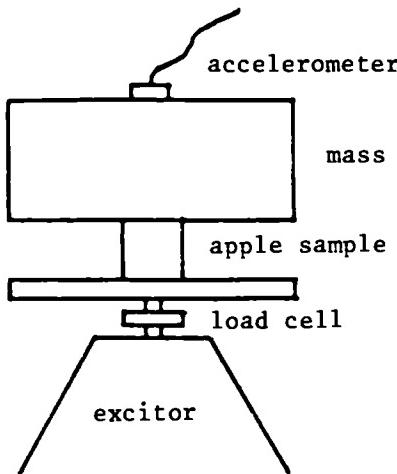


Fig. 1. Diagram of the destructive dynamic test arrangement.

When a force $f(t)$ is applied to this system, its dynamic equilibrium is described by the following differential equation in x (displacement) with respect to time t :

$$m\ddot{x} + c\dot{x} + kx = f(t) \quad (1)$$

Fourier transformation and rearrangement of this equation results in the acceleration frequency response function:

$$\frac{\ddot{X}(\omega)}{F(\omega)} = \frac{-\omega^2/k}{1 - \omega^2/\omega_n^2 + 2j\omega/\omega_n\zeta} \quad (2)$$

where $\ddot{X}(\omega)$ = Fourier transform of accelerometer signal, $F(\omega)$ = Fourier transform of force signal, ω = frequency, ω_n = natural frequency of system,

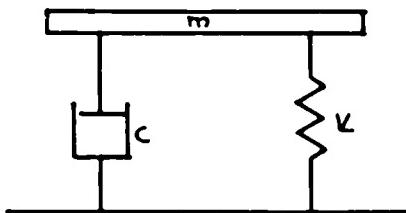


Fig. 2. Spring-damper-mass system corresponding to the experimental system shown in Fig. 1.

and ζ = damping ratio. This ratio of the Fourier transform of the accelerometer signal to that of the force signal is calculated by a structural dynamics analyser (HP 5423A). A transfer function, as shown in Fig. 3, is obtained, together with a value for the natural frequency f_n and the associated damping ratio ζ of the vibrating system.

From f_n and ζ , the spring constant k and the damping constant c can be calculated as

$$k = \omega_n^2 m \quad (3)$$

and

$$c = \zeta 2\sqrt{km} \quad (4)$$

Finally, the elastic modulus E and corresponding loss modulus E' of the sample are found from the equations

$$E = kl/A \quad (5)$$

and

$$E' = c\omega_n l/A \quad (6)$$

where l is the sample length and A is the area of the sample cross-section.

2.2. Non-destructive Dynamic Testing

2.2.1. Study of resonance of an apple

In this approach the apple can be considered as a mechanical system to be characterised by the relationship between the applied vibration and the

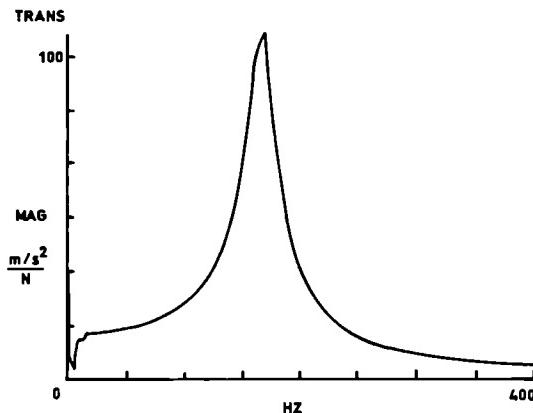


Fig. 3. Transfer function of a vibrating cylindrical apple sample loaded with a mass.

response of the fruit. The latter can be given as a frequency response function.

In order to relate the frequency response function to vibratory mode, two methods of modal analysis were used (van Woensel *et al.*, 1984). In the first, the apple was mounted on an electromagnetic exciter (B&K 4808). A low-mass accelerometer (2·4 g) was glued to the apple skin. In the second, the apple was suspended on a thin elastic string and excited by an impact hammer, an accelerometer being glued to the apple skin as before. Hence, in both cases the accelerometer was fixed and the excitation location was varied. By comparing the transfer functions obtained with both arrangements it is possible to find an additional resonant frequency (first resonant frequency) in the case where the first arrangement is used. Modal analysis was used to investigate further the fruit behaviour.

The mode shapes are shown in Fig. 4. Mode 1 is only found with the first arrangement. This mode is a so-called rigid-body mode of the structure (apple). Here the apple is not deformed, except near the point of support, where deformations occur due to the excitation force on the weak apple tissue.

Modes 2 and 3 are the spherical modes, which are important for this study. Two modes were found instead of one due to the fact that the apple is not a perfect sphere. The unique (theoretical) spherical mode splits up into two modes, corresponding to two principal axes of the apple cross-section. The more an apple differs from a sphere, the larger will be the difference between the resonant frequencies of modes 2 and 3.

It is concluded that caution should be exercised in interpreting the results of modal analysis tests, depending on the measuring arrangement. The connection between apple and exciter has a stiffening and damping effect on the dynamic behaviour of the apple. A rise of 5% in the resonant

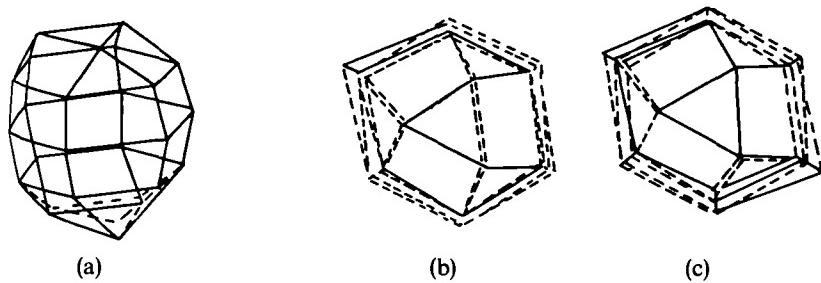


Fig. 4. Mode shapes obtained by modal analysis. (a) Mode 1: 329 Hz, side view; (b) mode 2: 663 Hz, view from above; (c) mode 3: 880 Hz, view from above.

TABLE 1
CORRELATION MATRIX

	<i>E</i>	<i>E'</i>	ζ	<i>f</i>	<i>S</i>	<i>S'</i>	ζ_c
<i>E</i>	1						
<i>E'</i>	0.947	1					
ζ	-0.414	-0.238	1				
<i>f</i>	0.926	0.912	-0.282	1			
<i>S</i>	0.918	0.921	-0.254	0.986	1		
<i>S'</i>	0.893	0.904	-0.179	0.982	0.899	1	
ζ_c	-0.783	-0.802	0.216	-0.912	-0.913	-0.728	1

frequencies was found. The same connection also caused an additional rigid-body mode, in this case at a resonant frequency of 329 Hz.

Following the derivations in a state-space approach on a theoretical model, a dynamic stiffness factor $S = f^2 m^{2/3}$, where f is the second resonant frequency and m the apple mass, can be derived (Cooke and Rand, 1973). This stiffness factor is related to the elastic modulus and Poisson's ratio for the fruit flesh.

2.2.2. Comparison of the results obtained by both methods

Forty Golden Delicious apples were tested over a wide range of maturity stages. Each apple was subjected first to a non-destructive resonance test. Thereafter cylindrical samples were cut from the apple and subjected to a vibration test.

In Table 1 the matrix of linear correlation coefficients between the measured system variables is given. High correlation coefficients exist between the elastic modulus derived from the destructive resonance test and all the variables from the non-destructive dynamic test.

The relationship between elastic modulus E and stiffness S is shown in Fig. 5. The correlation coefficient for a linear relationship is 0.981.

The damping ratio ζ_c derived from the non-destructive test correlates well with the elastic and loss moduli, E and E' , and with the resonant frequency f and the stiffness factor S .

The damping ratio ζ derived from destructive tests on cylindrical samples does not correlate well with any other system variable. This damping ratio was expected to be a measure of the presence of free water between the parenchyma cells of the apple tissue, a quantity which varies with the maturity of the fruit. This damping ratio is greatly influenced by the

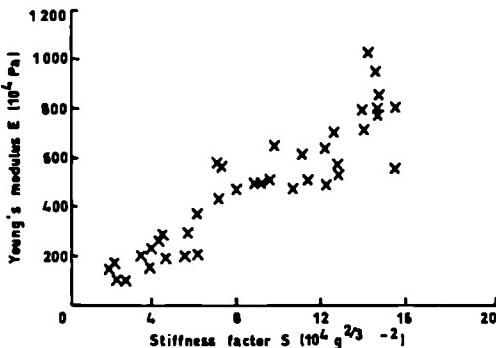


Fig. 5. Relationship between the elastic modulus E , obtained in a destructive dynamic test, and the stiffness factor S derived from a non-destructive dynamic test.

presence of a thin film of water between the apple sample and the loading mass or the vibrating plate.

2.2.3. Results from dynamic testing

Uniaxial compression and non-destructive resonance measurement were made at regular time intervals during three seasons on apples of the varieties Golden Delicious and Boskoop.

The stiffness factor in Fig. 6 shows a sharp decrease around the time the apples reach maximum maturity. It would appear that combining measurements of the stiffness factor with failure stress measurements gives

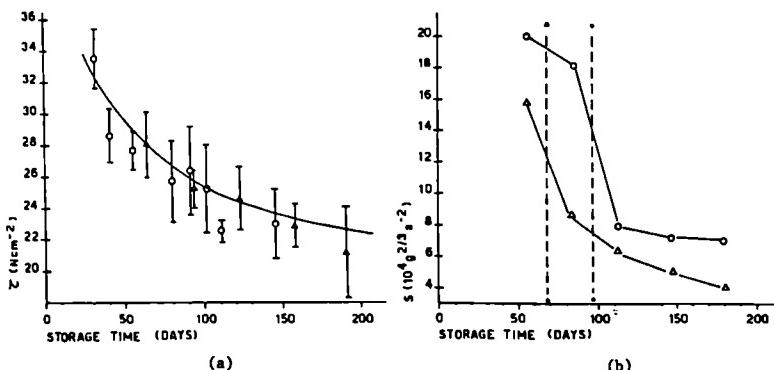


Fig. 6. (a) Compressive failure stress of cylindrical apple samples as a function of time. (b) Stiffness factor (from non-destructive dynamic test) as a function of time. (Δ , picked unripe; \circ , picked ripe. The dotted lines indicate biochemical maturity.)

good information about changes in fruit firmness and degree of maturity, and hence about the sensory acceptability to the consumer.

In another series of experiments consumer acceptability was determined using a series of subjective tests such as feeling, biting and tasting. A correlation matrix was constructed involving various mechanical properties as well as acceptability (van Woensel and de Baerdemaeker, 1985).

The dynamic elastic modulus in destructive tests and also the stiffness factor from tests on the whole fruit correlated well with the different acceptability groups, as shown in Fig. 7. It appears that there is a range of

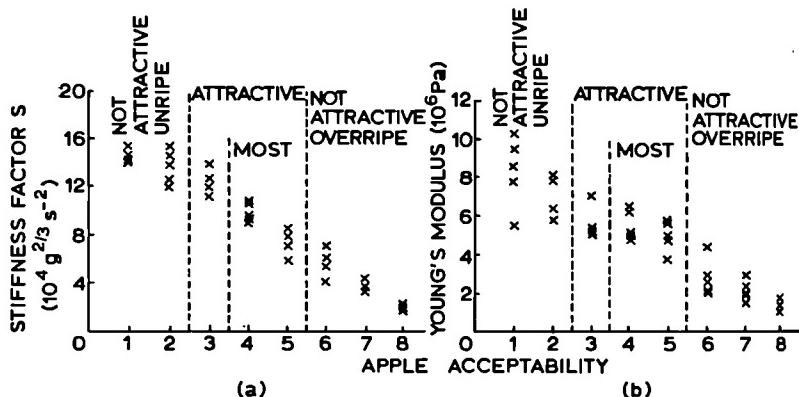


Fig. 7. (a) Dynamic stiffness factor related to apple acceptability to consumers.
 (b) Dynamic elastic modulus related to apple acceptability to consumers.

values for these measures for which the fruit is very likely to have good consumer acceptability.

2.3. Monitoring the Impact Force on the Fruit

The above-mentioned dynamic measurements attempt to characterise the mechanical behaviour of the fruit based on the measurement of input signals (force) as well as output signals.

A further simplification can be made if the input to the system is the dropping of the fruit from a known height on to a flat plate and the output is the resulting impact force. The latter is the only signal measured. This measurement method is illustrated in Fig. 8 (de Baerdemaeker *et al.*, 1982).

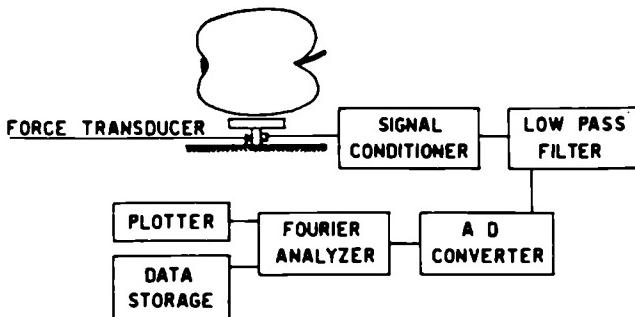


Fig. 8. Instrumentation for measuring the frequency spectrum of the impact force on a fruit.

The impact force can be studied in the time domain as well as in the frequency domain. An analysis in the frequency domain shows that more of the higher frequency components were present when the fruits were hard. This is shown in Fig. 9 (de Baerdemaeker *et al.*, 1982). Complete electronic processing of the impact force signal can give a rapid evaluation of fruit firmness. The firmness assessment based on this technique gives a local characteristic of the fruit, which in some cases may be insufficient because of the spatial variability of fruit properties.

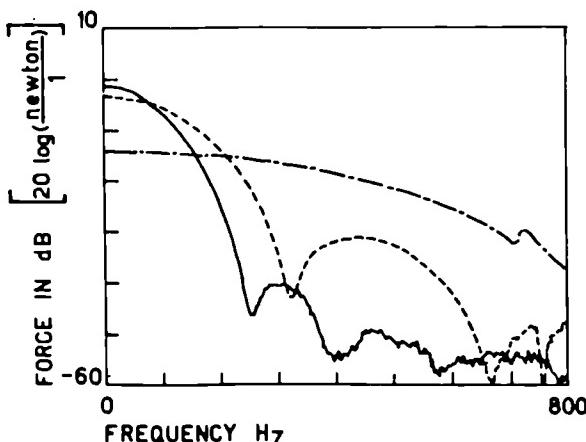


Fig. 9. Frequency spectra of the impact of: a rubber ball (alternating dots/dashes); a fruit with an elastic modulus of 2.15 MPa (dashed line); a fruit with an elastic modulus of 1.67 MPa (solid line).

3. SUMMARY

In this review some techniques were discussed for evaluation of fruit firmness based on dynamic measurements. The advantage of these techniques is that the required properties can be derived from short duration signals combined with appropriate signal processing. In this way their incorporation into sorting lines would make them suitable for industrial application.

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DISCUSSION

E. Rotstein: Recognising the influence on the mechanical properties of fruit such as apples of age, history, storage conditions, time of storage and maturity, should not more of these variables have been controlled in the collaborative trials? *J. de Baerdemaeker* agreed but explained that on that occasion, as it was impossible to provide all participants with standard samples, it was deliberately left to participants to purchase locally to see what kind of results emerged. *L. M. M. Tijskens*, who had analysed all the 'raw' results, said that it was quite clear from the original compression curves how fresh the apples were. The freshest were those bought and tested

in Denmark and showed the maximum force to be sustained long after fracture and the number of fragments produced to be few—2 or 3 at most. The oldest were evidently those bought and tested in France which showed a rapid decline in force after fracture and a large number of fragments. He estimated the latter to be at least 1 year old.

M. Kent was surprised that no compositional information had been given and related to the results on apples. Surely the water content was important? *de Baerdemaeker*, agreeing, said that the water content of properly stored apples did not change by more than 1 or 2%. There might have been some biochemical changes such as pectin bonding changes but these could not have been widely measured as the participating laboratories were, in the main, mechanical testing laboratories.

Collaborative Compression Tests on Gels

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SUMMARY

Compression tests on agarose and agarose-plus-sucrose gels were carried out by nine laboratories. Agarose powder was distributed to the participants and the gels prepared locally according to agreed instructions. Yield stress and deformability modulus values were calculated from the experimental force-deformation curves.

Results showed that such gels were not a good reference basis. Possible reasons for intra- and inter-laboratories differences are discussed.

INTRODUCTION

The results given and discussed in this chapter are a part of a collaborative exercise on mechanical properties of solid foods, carried out within the COST 90bis project by nine laboratories. The exercise consisted essentially of the application of compression tests to different products: apples, cheeses, meat products and agarose gels.

One of the objectives was to evaluate agarose gels as a model system for measurement of mechanical properties of real foods. This system was thought to have adequate characteristics to serve as a reference material. Hydrocolloid gels are, in general, homogeneous, easy to prepare and compatible with other materials such as simple food constituents incorporated in the gel structure, (Fiszman *et al.*, 1983). Structurally, hydrocolloid gels are formed by a tridimensional network with a more or less viscous medium embedded in it; interaction between them determines the mechanical behaviour of the system.

Compression tests are widely used to evaluate the mechanical characteristics of solid foods and constitute the basis of many empirical tests used to measure textural properties. The main condition for these tests to be rheologically valid is that the material under compression behave as a linear viscoelastic system. This is seldom the case. Another requisite is that no change in the initial geometry of the sample take place during the test. For these reasons, when obtaining force-deformation curves for gels or solid foods in general, it is not actually true deformation (unless at extremely small strains) but compression effects which are measured (Mohsenin and Mittal, 1977; Peleg, 1977). In these cases, the stress/strain ratio should not be identified as a modulus of elasticity but as a modulus of deformability (Bourne, 1979).

Results obtained in compression tests depend mainly on the structural characteristics of the material and on the experimental conditions of measurement. In particular, the dimensions of the sample, the rate of force application, and the magnitude of deformation must be carefully controlled when measuring, and adequately expressed when giving, the results of the test.

In this chapter, data reported by nine laboratories on yield stress and modulus of deformability values, obtained from experimental force-deformation curves, on 3% agarose and on 3% agarose-plus-30%-sucrose gels, are given and discussed.

EXPERIMENTAL

Materials: Agarose type I (low EEO) from Sigma (Product number A6013)
Sucrose.

Preparation of samples and measurement instructions: according to test specifications (see Appendix 1).

Distribution: the agarose powder was sent by post from the University College Dublin (Ireland) to each participating laboratory.

Participating laboratories: the laboratories taking part and the instruments used are listed in Table 1.

Not every laboratory was able to participate in every case. The details of the original results are given in Appendix 2. It was considered more appropriate to express maximum rupture strength as yield stress values rather than as maximum breaking force (F_{\max}) as initially established.

In general, participating laboratories submitted results that were

TABLE 1
PARTICIPATING LABORATORIES

<i>Laboratory</i>	<i>Code</i>	<i>Equipment used</i>
University of Nottingham, UK	NOTT	Instron Model 1140
SIK—The Swedish Food Institute, Gothenburg, Sweden	SIK	Instron Model 1122
Catholic University of Leuven, Belgium	LEUVEN	—
School of Professional Agricultural Engineers, Polytechnical University of Madrid, Spain	MADRID	Instron Model 1122
Sprenger Institute, The Netherlands	SI	—
Technical University of Denmark, Denmark	DEN	Instron Model 1140
University of Naples, Italy	NAPLES	—
Agrochemical and Food Technology Institute, Valencia, Spain	IATA	Instron Model 1140
Queen Elizabeth College, London, UK	QEC	Instron Model 1122

obtained according to the test specifications. However, some of them made the following modifications and additions:

- SIK: Dimensions of samples: cylinders of 16 mm diameter and 16 mm height.
- LEUVEN: Dimensions of samples: cylinders of 18 mm diameter and 17 mm height.
- SI: Two pieces of waterproof emery paper were inserted during measurement between the platens and the sample.
- DEN: Gelling was carried out in sausage skins producing slightly different diameters.
The prepared gels were stored 18 days before measuring.

Statistical treatment of the results: the data obtained in the participating laboratories in the collaborative study were introduced into a statistical programme for the determination of the mean value and the standard deviation, identification and elimination of outliers, and comparison of variances (Fig. 1). For elimination of outliers, Grubb's test was applied to each data set. For the evaluation of the homogeneity of the variances, the Bartlett test was applied (Commissariat à l'énergie atomique, 1978). When inhomogeneity was due to the results of only one laboratory, these were

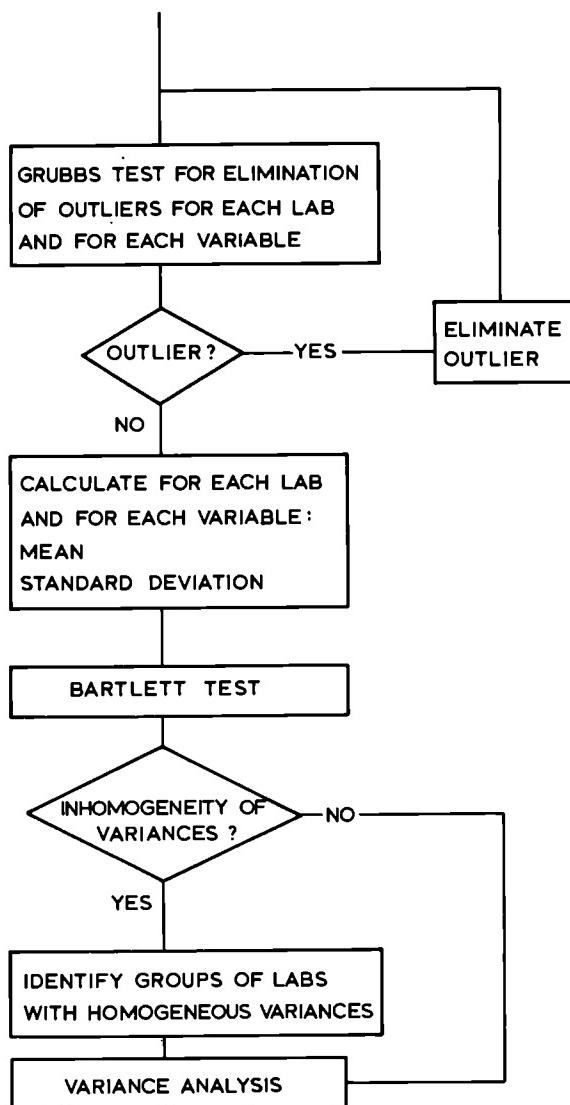


Fig. 1. Flow diagram of the statistical analysis.

eliminated and the analysis of variance was applied to the rest. When inhomogeneity was due to the results of two or more laboratories, groups of laboratories with homogeneous variances were made and analyses of variance applied separately to each group.

RESULTS

Agarose Gels

The application of the Bartlett test to the values given by the participating laboratories for both yield stress and deformability modulus, showed that the variances were not homogeneous (values of χ^2 were higher than those from tables; see Tables 2 and 3).

In the graphical arrangement of mean values of yield stress and the corresponding standard deviations (Fig. 2a), it can be seen that two groups of laboratories may be formed by examining the magnitude of the variances and that there exists a high variability among the mean values from all laboratories. Bartlett tests applied to each group confirmed that the one formed by NAPLES, IATA and SI and that formed by NOTT, MADRID, SIK, DEN, LEUVEN and QEC exhibited homogeneous variances within each group (Table 2).

TABLE 2
STATISTICAL ANALYSIS ON YIELD STRESS DATA OF 3% AGAROSE SAMPLES

Laboratory	\bar{x}	n	S_{n-1}	S_{n-1}^2	χ^2_{est} for all laboratories	χ^2_{est} for each group with homogeneous variances
NAPLES ^a	3.02	27	0.04	0.0018		
IATA	3.48	10	0.06	0.0040		3.26 ^c
SI	3.89	8	0.06	0.0041		
NOTT	2.92	5	0.13	0.0170		
MADRID	2.43	10	0.14	0.0201	64.68 ^b	
SIK	3.13	4	0.15	0.0225		4.03 ^d
DEN	3.22	19	0.16	0.0251		
LEUVEN	2.29	12	0.20	0.0408		
QEC	4.01	30	0.21	0.0451		

^aInitial n = 28, one outlier eliminated.

^bBartlett test, $\chi^2_{\text{tables}} = 15.51$.

^cBartlett test, $\chi^2_{\text{tables}} = 5.99$.

^dBartlett test, $\chi^2_{\text{tables}} = 11.07$.

TABLE 3
STATISTICAL ANALYSIS ON DEFORMABILITY MODULUS OF 3% AGAROSE SAMPLES

<i>Laboratory</i>	\bar{x}	<i>n</i>	S_{n-1}	S_{n-1}^2	χ^2_{est} for all laboratories	χ^2_{est} for each group with homogeneous variances
MADRID	10.81	10	0.40	0.1632		
IATA	13.52	10	0.42	0.1751		
NOTT	11.92	5	0.45	0.2020	36.93 ^a	9.49 ^b
QEC	16.10	30	0.56	0.3107		
DEN	12.86	19	0.68	0.4691		
NAPLES	11.64	28	0.88	0.7684		
LEUVEN	13.51	12	1.62	2.6172		

^a Bartlett test, $\chi^2_{\text{tables}} = 12.59$.

^b Bartlett test, $\chi^2_{\text{tables}} = 9.49$.

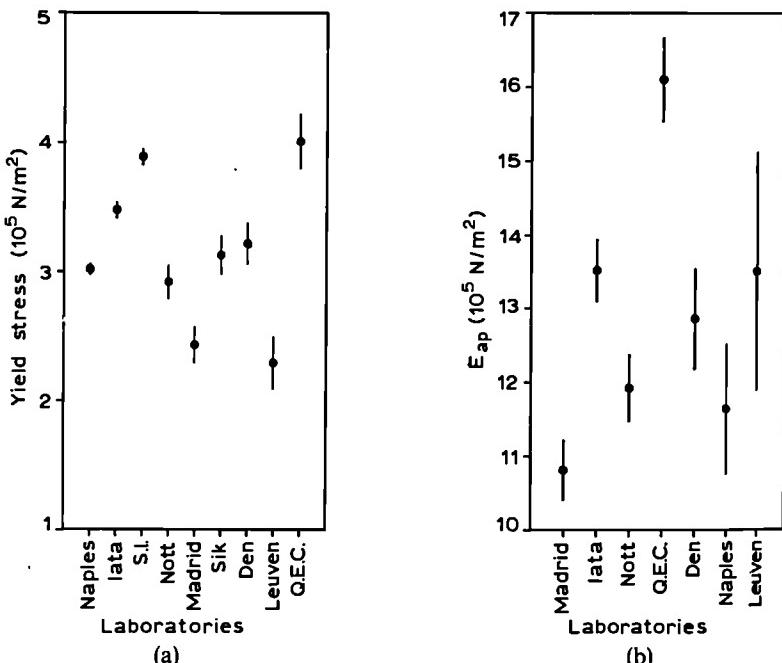


Fig. 2. Mean values and standard deviations of compression parameters for agarose gels: (a) yield stress; (b) deformability modulus.

Analysis of variance applied to each group of yield stress results showed that in both cases there were significant differences between the mean values at a probability level of 0·01;

$F = 970$ ($F_{\text{table}}: 5\cdot15$), and $F = 209$ ($F_{\text{table}} = 3\cdot26$) respectively

A similar analysis of deformability modulus data showed that for two of the laboratories (NAPLES and LEUVEN) variances were greater than for the other five (Fig. 2b). The Bartlett test confirmed that in this latter group variances were homogeneous (Table 3). The corresponding analysis of variance showed that in this group there were also differences between mean values significant at a level of probability of 0·01 ($F = 227$; $F_{\text{table}} = 3\cdot60$).

Variances of deformability modulus values were always greater than those of yield stress values.

Agarose-plus-Sucrose Gels

Analysis of the results obtained on 3% agarose gels to which 30% sucrose was added gave similar information to that obtained with agarose gels. There is inhomogeneity of the variances calculated for both properties considered (Tables 4 and 5).

Mean values of yield stress for these gels showed greater scatter than those for agarose gels, as can clearly be observed by comparing Fig. 3a with Fig. 2a.

TABLE 4
STATISTICAL ANALYSIS ON YIELD STRESS DATA OF 3% AGAROSE-PLUS-SUCROSE SAMPLES

Laboratory	\bar{x}	n	S_{n-1}	S_{n-1}^2	χ^2_{est} for all laboratories	χ^2_{est} for each group with homogeneous variances
IATA	5·75	10	0·05	0·0028		
NAPLES	3·22	12	0·08	0·0057		1·47 ^b
SI	6·43	7	0·08	0·0057	58·58 ^a	
DEN	5·08	17	0·28	0·0778		
NOTT	4·65	6	0·31	0·0950		
QEC	4·25	30	0·31	0·0971		4·41 ^c
SIK	3·38	4	0·42	0·1758		
LEUVEN	6·46	19	0·44	0·1925		

^aBartlett test, $\chi^2_{\text{tables}} = 14·06$.

^bBartlett test, $\chi^2_{\text{tables}} = 5·99$.

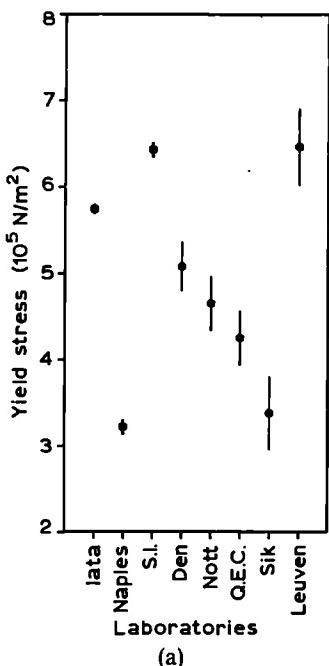
^cBartlett test, $\chi^2_{\text{tables}} = 9·49$.

TABLE 5
STATISTICAL ANALYSIS ON DEFORMABILITY MODULUS DATA OF 3% AGAROSE-PLUS-SUCROSE SAMPLES

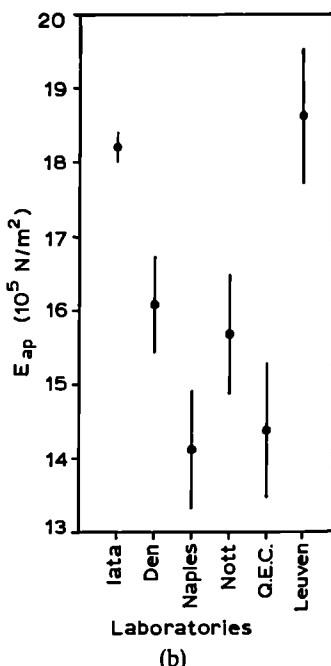
Laboratory	\bar{x}	n	S_{n-1}	S_{n-1}^2	χ^2_{est} for all laboratories	χ^2_{est} for each group with homogeneous variances
IATA	18.20	10	0.20	0.0400		
DEN	16.08	17	0.64	0.4140		
NAPLES	14.12	12	0.79	0.6293	18.63 ^a	
NOTT	15.68	6	0.80	0.6457		2.42 ^b
QEC	14.38	30	0.90	0.8120		
LEUVEN	18.63	19	0.90	0.8178		

^a Bartlett test, $\chi^2_{\text{tables}} = 11.07$.

^b Bartlett test, $\chi^2_{\text{tables}} = 9.49$.



(a)



(b)

Fig. 3. Mean values and standard deviations of compression parameters for agarose-plus-sucrose gels: (a) yield stress; (b) deformability modulus.

Looking at Fig. 3a, two groups showing apparently similar variances can be identified: one formed by three laboratories (IATA, Naples and SI) and one formed by the other five. This was confirmed by the corresponding Bartlett tests (Table 4). Here, also, the analysis of variances showed that in both groups there are significant differences between mean values at $\alpha = 0\cdot01$ with $F = 7735$ ($F_{\text{table}} = 5\cdot57$) and $F = 144\cdot9$ ($F_{\text{table}} = 3\cdot60$) respectively.

In the case of the deformability modulus (Table 5, Fig. 3b), the elimination of data from one laboratory (IATA) allowed the formation of a group of five laboratories showing homogeneous variances, and within which there were also significant differences between mean values ($F = 92\cdot6$; $F_{\text{table}} = 3\cdot58$).

In these gels also, variances of deformability modulus data were greater than those for yield stress.

CONCLUSIONS

1. Hydrocolloid gels are not a good reference material for standardisation of compression tests for solid foods mainly because of difficulties in preparing samples which can be relied on to possess the same characteristics.
2. The larger variance values found in the results from some laboratories may be attributed to several factors: poor control of sample dimensions, plane surfaces of samples not being perfectly parallel to one another and to the platens, and differences in ambient temperature and relative humidity at the time of measurement. In the case of the deformability modulus, lack of precision in measuring the slope of the force-deformation curve is an important additional factor.
3. Significant differences between mean values may be attributed to: differences in the quality of the water used to prepare the gels, differences in the method of preparing them, particularly the heating and cooling pattern, the replacement of water lost by evaporation, the completeness of dispersion of agarose and dissolution of sucrose. Although of less importance, the influence of differences in the measuring system and in the ambient conditions of measurement should also be considered.

Within-laboratory repeatability depends largely on the skill and experience of the operator in preparing and measuring gels. Reproducibility of results between laboratories depends mainly on the correct

identification and control of the contextual factors affecting the measurement; these would be easier to ensure if the reference material were a well-defined, homogeneous one, centrally-prepared.

ACKNOWLEDGEMENTS

We are indebted to the participating laboratories, to Professor R. Jowitt for his valuable comments, to Mr López Santoveña for his help in statistical analysis of data and to CAICYT (Science and Technology Research Commission) for financial support.

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APPENDIX 1: INSTRUCTIONS FOR PREPARING AND MEASURING MECHANICAL PROPERTIES OF AGAROSE GELS

- Gels: (A) Agarose gels of 3% agarose;
(B) Agarose gels of 3% agarose plus 30% sucrose.

Preparation of gels: (A) Disperse the agarose powder provided in distilled water and heat slowly until completely dissolved. Allow to stand and to cool at room temperature until gel forms. (B) Idem but first dissolving the sucrose in the distilled water before addition of the agarose.

In both cases, replace any evaporated water to maintain initial concentration.

Forming of samples: two alternative procedures may be used:

Either: 1. Store gels for at least 24 h at 4–6°C and 100% RH before cutting.

Cut cylinders of 17 mm diameter and 17 mm height using a stainless-steel corkborer and the cutting procedure described in Fig. A.1.

Cylinders should be at room temperature ($20 \pm 2^\circ\text{C}$) for property measurement.

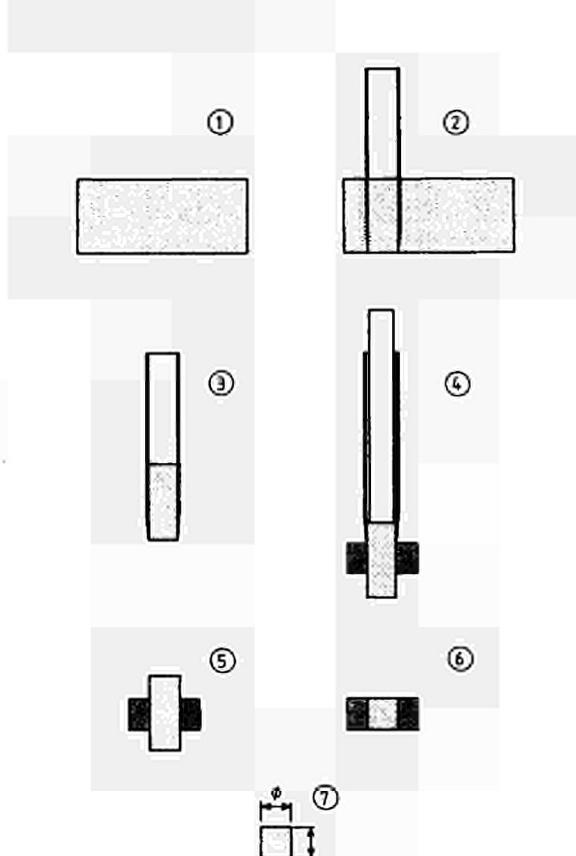


Fig. A.1. Procedure to obtain cylindrical probes: (1) gel, (2) cutting with corkborer, (3) corkborer with cut cylinder inside, (4) expelling the gel with a rod into a cylindrical hole in a steel die, (5) gel cylinder in position for cutting, (6) sample cut with a thin razor blade, (7) sample ready for measurement.

Or:

2. Fill the hot solution, before it gels, into 'sausage skins' and allow it to cool down at room temperature.
- Store gels for at least 24 h at 4–6°C and 100% RH before cutting.
- Cut cylinders of 17 mm height and test at room temperature ($20 \pm 2^\circ\text{C}$).

Measuring conditions:

Compression rate: 50 mm min^{-1} .

Paper speed: 1000 mm min^{-1} .

Plunger diameter greater than sample diameter.

Instron UTM or similar.

Compression test to rupture.

Properties:

Rupture force (F_{\max}).

Deformability modulus (E_{app}).

(see Fig. A.2).

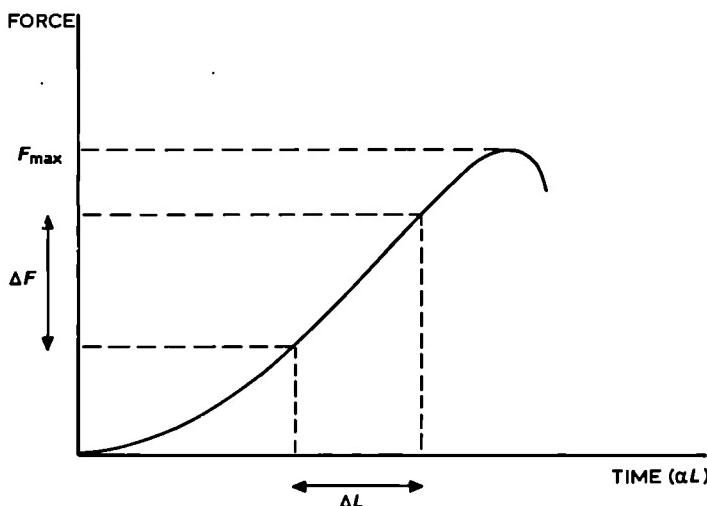


Fig. A.2. Force-deformation curve

$$F_{\max} = \text{Rupture force} \quad E_{\text{app}} = \frac{L_0}{S} \frac{\Delta F}{\Delta L}$$

APPENDIX 2:

INDIVIDUAL YIELD STRESS RESULTS FOR 3% AGAROSE
GEL CYLINDERS(N m⁻² × 10⁻⁵)

IATA	3.5	3.5	3.5	3.5	3.5	3.5	3.4	3.4	3.4	3.6
NAPLES	3.0	3.0	3.0	3.0	3.0	3.0	3.1	3.0	3.0	3.0
	3.0	3.0	3.0	3.0	3.1	3.0	3.0	3.0	3.1	3.0
	3.1	3.0	3.0	3.1	3.1	3.0	3.0	3.2		
NOTT	3.0	3.0	2.7	2.9	3.0					
MADRID	2.2	2.4	2.5	2.5	2.6	2.5	2.4	2.6	2.4	2.2
QEC	4.2	4.1	4.3	4.0	4.2	4.0	3.8	3.8	3.6	3.8
	4.2	4.1	4.3	4.1	3.9	3.9	4.0	3.9	4.1	4.1
	3.9	3.8	3.5	4.3	4.2	4.3	4.2	3.8	3.8	4.1
DEN	3.2	3.1	3.4	3.4	3.3	3.5	3.4	3.1	3.0	3.1
	3.1	3.5	3.3	3.0	3.2	3.1	3.2	3.2	3.1	
SIK	3.0	3.0	3.3	3.2						
SI	3.8	3.9	3.8	3.9	3.9	3.9	4.0	3.9		
LEUVEN	2.3	2.2	2.3	2.6	2.1	2.1	2.0	2.1	2.5	
	2.4	2.3	2.6							

INDIVIDUAL DEFORMABILITY MODULUS RESULTS FOR 3%
AGAROSE GEL CYLINDERS(N m⁻² × 10⁻⁵)

LEUVEN	13.7	13.2	13.6	17.3	13.0	14.6	11.3	12.3	12.2	12.9
	12.6	15.4								
IATA	13.5	13.5	13.2	13.2	13.2	13.9	14.4	13.2	13.2	13.9
NAPLES	10.5	10.7	12.5	10.7	12.2	12.2	12.2	12.4	12.4	13.0
	12.4	12.4	10.7	10.7	11.5	11.5	11.3	10.7	11.5	11.3
	11.5	11.0	10.9	12.7	13.0	11.0	13.0	10.0		
NOTT	12.0	12.1	11.3	11.7	12.5					
MADRID	10.6	10.5	10.8	10.8	11.6	10.6	10.2	11.3	10.7	11.0
QEC	16.54	16.31	16.09	16.09	15.87	16.09	16.54	16.78	16.09	15.66
	15.87	17.02	16.31	15.45	16.31	16.09	16.54	15.25	15.45	15.66
	15.66	15.45	14.86	17.02	16.31	16.78	16.54	15.25	15.66	16.54
DEN	14.27	12.03	13.02	13.62	13.80	13.62	13.37	12.16	12.57	12.48
	11.83	13.56	12.25	12.19	12.79	12.50	12.79	12.72	12.83	

**INDIVIDUAL YIELD STRESS RESULTS FOR 3% AGAROSE-
PLUS-SUCROSE GEL CYLINDERS**

(N m⁻² × 10⁻⁵)

IATA	5.7	5.7	5.7	5.8	5.8	5.8	5.8	5.8	5.7	5.7
NAPLES	3.3	3.3	3.2	3.2	3.1	3.2	3.3	3.3	3.1	3.2
	3.2	3.3								
NOTT	4.8	4.8	5.0	4.1	4.6	4.6				
QEC	4.4	4.4	4.1	4.6	3.7	4.5	4.5	4.4	4.0	4.2
	4.1	3.4	3.9	4.6	4.2	3.8	4.3	4.5	4.5	4.1
	4.0	4.2	4.2	4.0	4.6	4.1	4.5	4.7	4.4	4.7
DEN	4.9	5.5	5.5	5.1	5.3	5.1	5.3	5.2	5.2	5.2
	5.0	5.1	5.1	4.5	4.7	4.6	5.1			
SIK	3.4	3.8	3.5	2.8						
SI	6.4	6.4	6.4	6.4	6.6	6.4	6.4			
LEUVEN	5.3	6.0	6.1	6.2	6.2	6.3	6.4	6.4	6.4	6.4
	6.5	6.5	6.5	6.5	6.6	6.6	6.9	7.1	7.1	7.2

**INDIVIDUAL DEFORMABILITY MODULUS RESULTS FOR 3%
AGAROSE-PLUS-SUCROSE GEL CYLINDERS**

(N m⁻² × 10⁻⁵)

IATA	17.9	17.9	18.2	18.2	18.2	18.2	18.5	18.2	18.2	18.5
NAPLES	15.0	15.3	14.9	14.4	14.4	13.4	14.0	14.1	14.7	13.1
	13.1	13.1								
LEUVEN	18.8	19.1	17.5	17.9	18.4	20.3	17.4	20.2	18.8	18.9
	18.6	17.1	18.8	18.9	17.9	18.3	18.2	18.7	20.2	
NOTT	15.4	15.0	16.1	14.6	16.5	16.5				
QEC	15.25	14.86	14.15	15.87	13.20	14.32	14.50	13.98	14.15	14.32
	14.86	14.15	13.05	13.20	14.50	14.68	12.23	12.90	16.09	13.82
	13.58	14.15	14.68	14.68	14.32	14.68	15.25	15.25	14.68	15.87
DEN	15.28	16.05	17.45	15.77	16.69	16.64	16.58	16.38	16.49	16.38
	16.05	15.88	15.91	14.50	15.63	15.77	16.05			

DISCUSSION

R. Jowitt observed that it was not, after all, surprising that gels made up by participants themselves, albeit according to precise instructions from centrally-supplied high-quality agarose powder, displayed substantial

differences in mechanical properties. The exercise seemed to confirm nicely that a common reference material must always be supplied from a common, single source so as to ensure at least its *initial* uniformity. That is one of the essential *raisons d'être* of the Community Bureau of Reference which provides a variety of certified reference materials in Europe, soon to include some relevant to foods. *A-M. Hermansson* commented that agarose gels were prone to syneresis and friction effects to which *L. Duran* replied that no syneresis had been observed during these tests.

Compressibility Characteristics of Food Powders: Characterising the Flowability of Food Powders by Compression Tests

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SUMMARY

Shear tests are a generally-accepted method for judging the flowability of particulate materials. However, such measurements require special equipment and are laborious and time-consuming. The validity of the simple compression test proposed by Peleg was proven by him for only a limited number of materials. Such a test would provide a convenient method for any laboratory where a materials testing machine is already available. The suitability of different types and sizes of compression test cells for food powders was studied. Copies of such cells were also sent to other laboratories for comparative studies. Finally, an improved version together with standardised samples of particulate foods—essentially wheat products—were sent to the participating laboratories. The results of the compression tests showed a significant correlation with the results from shear tests and were reproducible between laboratories. The test gives only approximate measures of the flowability of powders but may be very useful for comparing flowability between different samples of a particular product, e.g. for the purpose of process control.

INTRODUCTION

Yield loci from shear tests are generally accepted as a scientifically-based method of judging the flowability of particulate materials. However, such measurements require special equipment and are laborious and time-consuming. Consequently, a simple compression test was proposed by

Peleg (1971), who also proved its validity for a limited number of food materials.

In order to determine the validity of such compression tests, a range of particulate foods has to be studied and the correlation between compressibility and flowability established. Furthermore, the reproducibility of the modified and standardised compression tests has to be shown, when used at different laboratories, by personnel not familiar with or trained in the measurement of the properties of bulk solids.

Under the COST 90bis programme the following approach was taken: as a first step a copy of Peleg's compression cell was built and its general suitability for measurements on foods was established. At the authors' institute the suitability of compression tests for particulate foods was studied in more detail and the results were correlated with data from shear experiments. At the same time, four copies of the compression cell, together with food samples, were sent to the participating laboratories and the results were compared with those from the authors' laboratory. This resulted in a modification of the instructions for using the Peleg cell, and the improvement thus achieved was proven by a ring experiment on further food particulates. From the pooled efforts the general validity of the methods can be judged and a further modification to the compression cell—to be studied in future experiments—was proposed.

METHODS

Shear tests with an instrument according to Jenike are generally accepted (Jenike, 1970) while comparable measurements can also be obtained using an annular shear cell (Münz, 1976). From the yield loci two quantities are estimated: unconfined yield strength, f_c , and major consolidating stress, σ_1 (Fig. 1). A flow function quantity, f_{fc} , may be used to characterise flowability (Table 1) (see also Schubert, 1987). Shear tests were carried out

TABLE 1
CHARACTERISING FLOWABILITY

<i>Flowability</i>	<i>Flow function, f_{fc}</i>	<i>Compressibility, b_{10}</i>
Non-flowing	< 2	> 0.02
Cohesive	< 4	> 0.06
Easy flowing	< 10	> 0.10
Free flowing	> 10	

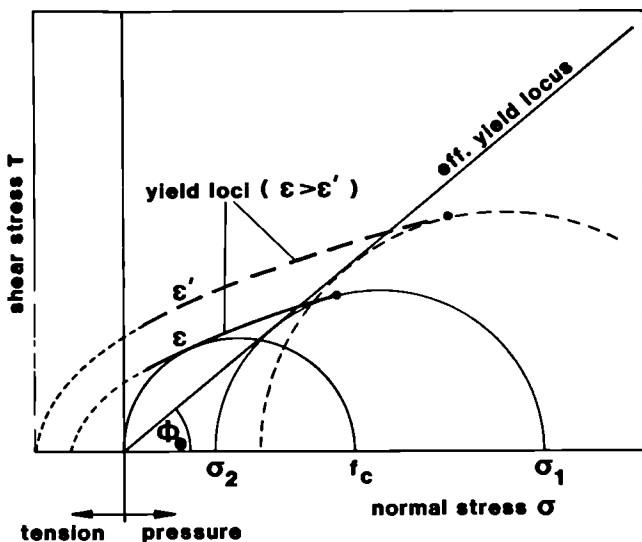


Fig. 1.

on several particulate foods (Ehlermann, 1985), which were also used for the comparisons reported here.

No details regarding the dimensions of the Peleg compression cell and no instructions for its use were available. However, the diameter and the filling height were each assumed to be 40 mm (Fig. 2). Identical compression cells were sent to the participants (Table 2) in the ring experiment. It became quite clear during initial experiments that friction between the piston and the measuring cell wall was the main cause of erroneous results. Using similar cells of different scale (see legend to Fig. 2) the influence of the cell size could be studied. Additionally, for the larger cell of 80 mm diameter a special piston was provided (Raschka, 1986). By using strain gauges on the inner part of the piston to measure the pressure directly at the powder surface, this facilitated the separation of the effects of wall friction from

TABLE 2
LABORATORIES PARTICIPATING IN THE COST 90bis POWDER EXPERIMENTS

-
1. Agricultural and Food Engineering Department, University College, Dublin, Ireland (McKenna)
 2. SIK—The Swedish Food Institute, Gothenburg (Hermannson)
 3. Sprenger Institute, Wageningen, The Netherlands (Tijskens)
-

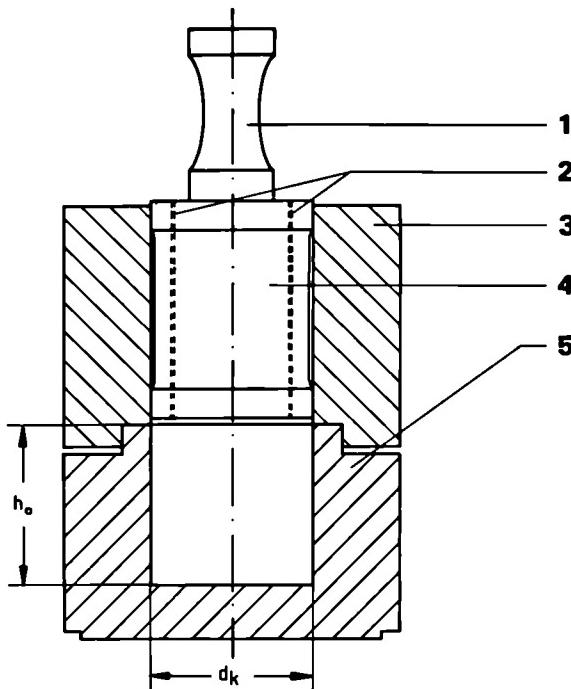


Fig. 2. Compression cell according to Peleg. 1, Pressure knob; 2, air outlets; 3, auxiliary guideway; 4, piston; 5, powder container/compression cell.

<i>Cell model number</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>
Initial height of powder h_0 and piston diameter d_k (mm)	20	40	80	$\frac{28}{\sqrt{2}}$
Scale-up factor	1	2	$4\sqrt{2}$	
Piston/cylinder clearance (μm)	13	18	22	21

those of true pressure on the surface of the consolidated powder (Fig. 3). It was confirmed (Ehlermann and Raschka, 1986) that the modified version gave correct, reliable measurements.

For the evaluation of compression experiments several functions have been proposed. Peleg (1977) proposed a semi-log approach:

$$\rho_{\text{bulk}} = a^* + b^* \ln(p/p_0) \quad (1)$$

where ρ_{bulk} = bulk density, a^* = constant, b^* = compressibility (related to ρ_{bulk}), p = pressure and p_0 = reference pressure (e.g. $p_0 = 1 \text{ Pa}$).

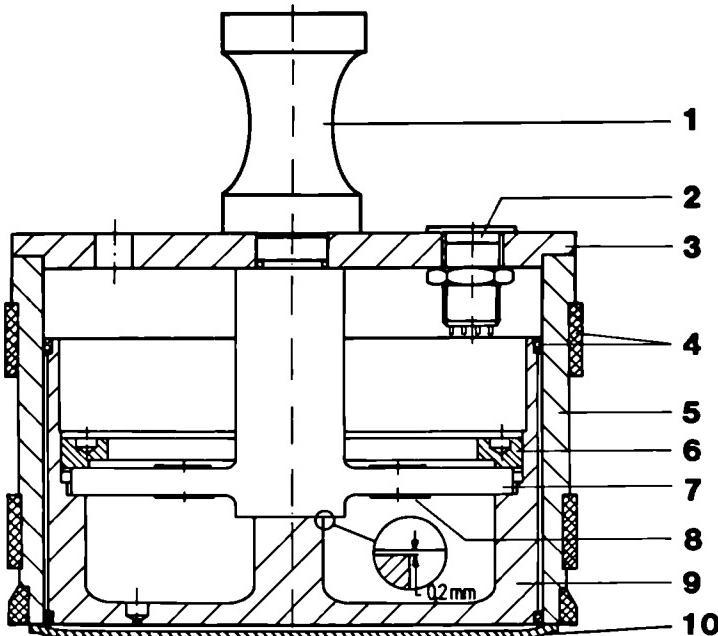


Fig. 3. Device for measuring piston pressure; used with compression cell model no. 3 in place of the standard piston. 1, Pressure knob; 2, miniature receptacle; 3, cover; 4, PTFE rings; 5, guideway; 6, threaded ring; 7, beam; 8, resistance strain gauges; 9, piston; 10, thin foil (drawn to an enlarged scale in the figure).

During a compression test the displacement of the piston and the consolidating force are recorded. Using the dimensions of the compression cell and the mass of the sample, the actual bulk density can be calculated by

$$\rho_{\text{bulk}} = m_s/[A(h_0 - x)] \quad (2)$$

where m_s = mass of the sample, A = surface area of the piston, h_0 = initial filling height and x = displacement of the piston.

Most of the food powders used by Peleg (1971) have a solid density of about 1500 kg m^{-3} and the comparison of compression tests on powders of similar solid density is reasonable. Using the relation between porosity ε and the solid density ρ_s of the particles

$$1 - \varepsilon = \rho_{\text{bulk}}/\rho_s$$

eqn. (1) can be made independent of particle density:

$$1 - \varepsilon = m_s/[\rho_s A(h_0 - x)] = a + b \ln(p/p_0) \quad (3)$$

where $a = \text{a constant}$ and $b = \text{compressibility}$ (if logarithm is to base 10, b_{10}). Hence the compressibility b or b_{10} is determined by the slope of the function $1 - \varepsilon = f[\ln(p/p_0)]$ or $f[\log(p/p_0)]$, respectively.

A typical compression curve is shown in Fig. 4. During the initial phase the surface of the piston comes into contact with the surface of the bulk material. There is practically no change in porosity during this phase and the powder is not yet flowing. During Phase II the large voids between particles are eliminated by rearrangement of the particles, breaking the material bridges above them. Large pores between particles which cause loose packing are characteristic of cohesive powders. The loose structure of uncompressed powders is due to interparticle adhesion. As this is also the reason for poor flowability of cohesive powders it is logical that compressibility be correlated with flowability. Thus Phase II defines the range of pressures of most interest for correlation of the results of a compression test with those of a shear test. During Phase III the further reduction in volume is achieved by moving and rearranging the particles in small regions. During this final phase a comminution of the particles occurs and a consolidated tablet results. The pressure range of Phase III is much greater than that occurring under practical conditions of food storage.

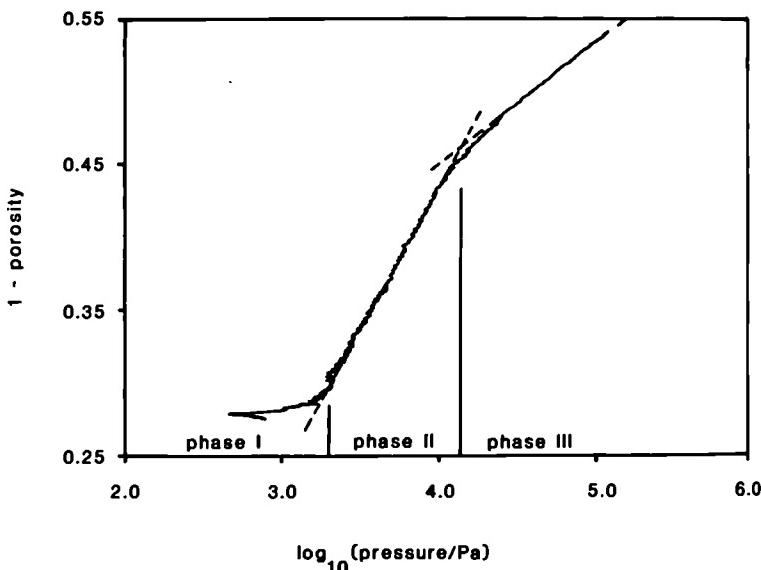


Fig. 4. Typical form of a compression curve for wheat flour type 405 (household) using compression cell model no. 2.

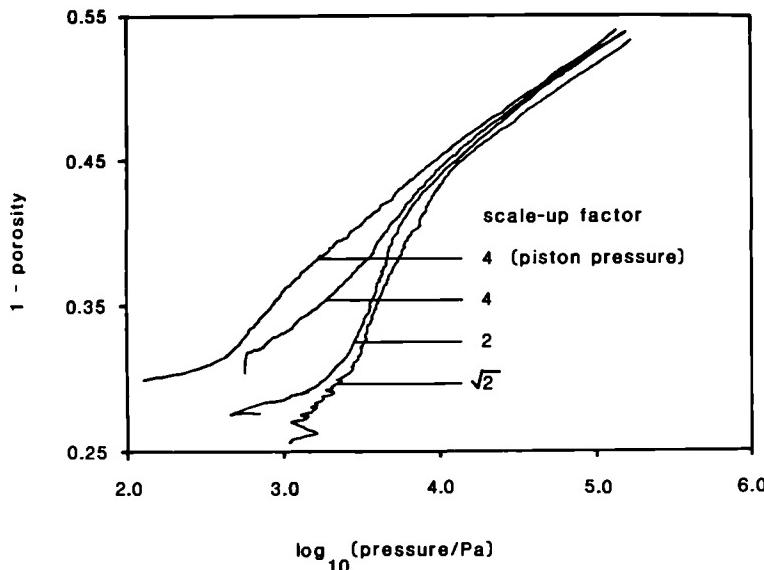


Fig. 5. Comparison of compression curves for wheat flour type 405 (household) obtained with the various compression cells (see text for explanation).

However, many compression tests are reported in this pressure range and the analytical functions proposed elsewhere to evaluate such measurements are only valid at higher stresses.

With the help of the modified piston (Fig. 3) the influence of friction between piston and cell wall could be removed and the resulting compression curve is closer to a straight line than that from conventional measurement methods (Fig. 5). With increasing size of the measurement cell the contribution of friction decreases and the curves approach that of the friction-free model.

The evaluation of compression measurements should differentiate between Phases II and III. The slope of Phase II will approach the slope determined with the friction-free cell as a limiting value for very large cells.

MATERIALS

In order to establish the validity of such compression tests, a wide range of materials, exhibiting good to very poor flowability, was tested. The materials included limestone of various particle sizes, size-distribution and

moisture content, powdered sugar, semolina and flours of several types. For the comparison under the COST 90bis programme wheat flour of household type 405, 'middlings' and 'clears', were used. The materials were obtained from a nearby mill and divided amongst the participants.

RESULTS OF COMPRESSION TESTS

Compression and yield loci tests were conducted on a variety of materials. As more shear measurements by the annular shear cell were available, only these values were finally compared to those of the compression tests. It is well known that measurements with the Jenike cell yield values for cohesion and unconfined yield strength that are larger, by a factor of 2 to 4, than those determined with the annular shear cell. The most suitable quantity to describe flowability is the flow function defined by Jenike (1970):

$$f_{fc} = \sigma_1/f_c \quad (4)$$

where σ_1 = major consolidating stress and f_c = unconfined yield strength.

Figure 6 shows compressibility (i.e. the slope of Phase II in Fig. 4) versus the reciprocal of the flow function. The annular cell measurements are corrected by a factor 3 to the Jenike measurements. Linear regression yields a line of reasonably good fit ($r = 0.82$).

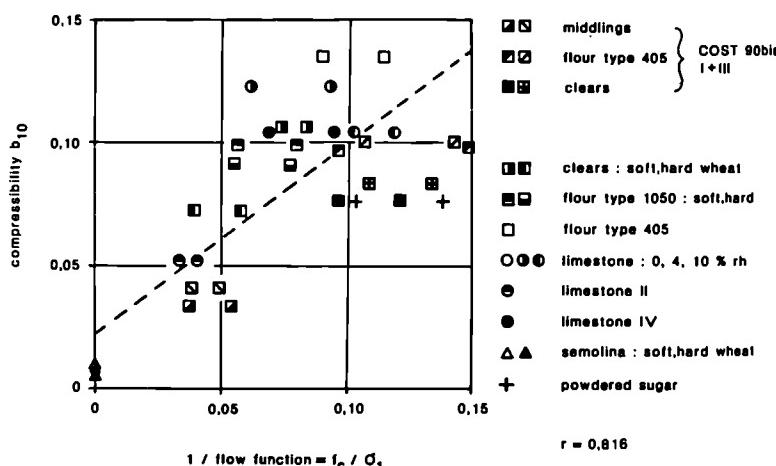


Fig. 6. Compressibility (logarithm to base 10) versus the reciprocal of the flow function for a variety of powders.

For many cohesive powders, the shear test yields different yield loci for the various major consolidating stresses applied. Hence, flow function values will vary with the type of consolidation load. Most of the measurements reported here used stresses of 4 and 6 kPa, consequently Fig. 6 shows two values for the flow function and one value for the compressibility for each product.

Slope and intercept in Fig. 6 imply that compressibility b_{10} and reciprocal flow function are of approximately the same value. However, from the experience gained with these materials, values corresponding to those in Table 1 will describe more realistically the flow behaviour of most materials.

COST 90bis COLLABORATIVE STUDY

As mentioned above, the initial trials in the participating laboratories (Table 2) were not satisfactory. The instructions for use of the compression cell had to be revised in order to ensure proper handling and measurement. A repetition, with some guidance on the expected behaviour of the distributed samples, resulted in values which approached our own (Table 3). This proves that the proposed method is easy, reliable and robust enough to be used at different places where little detailed experience of measurements on bulk solids is available. A further round of the ring experiments is still in progress. It is expected that the additional results will confirm these preliminary findings.

TABLE 3
COMPRESSIBILITY b_{10} OF FLOUR TYPE 405 AS DETERMINED BY THE PARTICIPATING LABORATORIES

b_{10}	Standard deviation	Regression coefficient	Source
0.080	0.0015	Special cell	Reference laboratory
0.071		0.888 Phases II and III	
0.138		0.998 Phase II only	Participating laboratories
0.079		0.98 Phase II only	

CONCLUSIONS

A simple compression test on powdered foods can be conducted in any food laboratory with access to a force/deformation testing machine.

Compressibility is a quantity characterising to some extent the flowability of bulk particulate solids. As the results from materials of different composition cannot be compared, each food variety requires a set of reference measurements. From these data the validity of the approach can be estimated and the range of reliability can be established. During the experiments it became obvious that several improvements to the details of the test cell would increase the value of the method. This has to be proven in future experiments.

The simple compression test only gives an approximate measure of the flowability of powders. It is not suitable for silo design but may prove to be a convenient method for process control of particulate materials.

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Interpretation of Stress Relaxation Curves: Some Theoretical and Practical Aspects

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SUMMARY

The first part of this chapter briefly reviews some simple basic aspects of linear stress-relaxation behaviour. Results obtained by Comby et al. (1985) in compression testing of high-methoxyl pectin gels and published in tabulated form are analysed along these lines. As most experimental measurements are not in the linear range, two equations are compared in the second part of the chapter: the empirical equation proposed by Peleg (1979, 1980) and a semi-empirical equation for describing stress relaxation in viscoelastic liquids obeying a power-law in steady flow regimes (Launay, 1979, in press). Experimental results obtained in compression testing of three food samples (apple and potato flesh, cooked cheese) indicate that the latter equation fits better than the former. It is shown that, for both equations, frequency of data sampling has a significant effect on fit terms. The limiting force value calculated from Peleg's equation depends on the duration of stress relaxation and has probably no rheological meaning. The prevailing solid- or liquid-like character of a food material seems to be related to the value of exponent n in the power-law equation. However, the proper evaluation of the long-term equilibrium modulus of a viscoelastic solid remains unanswered in the case of biological materials.

1. INTRODUCTION

Compression testing of solid food products is now used routinely in many laboratories for specification control, instrumental texture evaluation, etc. If the compression test is limited to small deformations, it is very easy to

obtain a relaxation curve by stopping the cross-head when a predetermined value of the force or of the distance is reached (constant strain). The latter experimental condition is more easily satisfied with the required precision than the former, particularly at high compression rates. The shape of the stress relaxation curve gives qualitative information on the viscoelastic properties of the compressed sample. However, much of this information is often wasted because simple interpretation methods are not available. The aim of this chapter is twofold: first, to present briefly the classical interpretation of stress relaxation in the linear case using tabulated data published in a paper by Comby *et al.* (1985) to illustrate some of the points; secondly, empirical data-fitting for non-linear behaviour will be discussed and two simple equations will be compared using some of the authors' own experimental results.

2. LINEAR VISCOELASTIC BEHAVIOUR

Many textbooks may be consulted for a thorough understanding of this topic and, among them, Ferry's (1980) work is certainly one of the most popular, even if it is devoted to polymers.

In the linear case, the basic building block used to describe stress relaxation phenomena is the Maxwell element (Fig. 1a). At constant strain

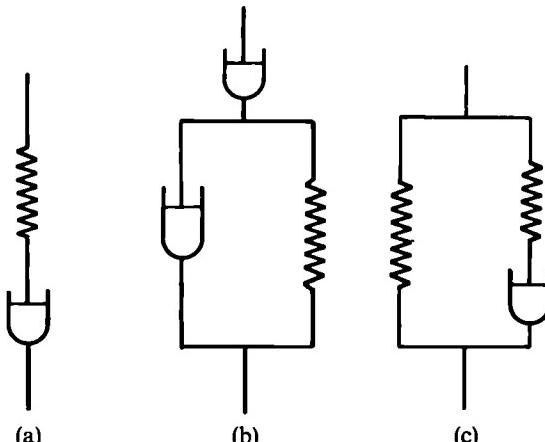


Fig. 1. Some simple analogue representations of linear viscoelastic behaviour. (a) Maxwell model; (b) Lethersich model; (c) solid viscoelastic behaviour.

the stress σ decays as a function of time t from σ_0 at the beginning of relaxation to 0, according to eqn. (1):

$$\sigma = \sigma_0 e^{-t/\tau} \quad (1)$$

where $\tau = \eta/E$ is the relaxation time. This behaviour is typical of a viscoelastic liquid because the stress relaxes completely. If the stressing time, Δt , preceding relaxation is shorter than τ (say $\Delta t \leq 0.2\tau$), eqn. (1) takes the form

$$\sigma = E\varepsilon e^{-t/\tau} \quad (2)$$

where ε is the fixed strain. In that case the stress relaxation modulus, $E_{(t)}$, is independent of ε :

$$E_{(t)} = \sigma_{(t)}/\varepsilon = E e^{-t/\tau} \quad (3)$$

If n relaxation mechanisms are involved, n Maxwell units may be combined in parallel:

$$\sigma = \sum_{i=1}^{i=n} \sigma_{0,i} e^{-t/\tau_i} \quad \text{where} \quad \sum_{i=1}^{i=n} \sigma_{0,i} = \sigma_0 \quad (4)$$

If Δt is less than the shortest relaxation time τ_n , eqn. (5) is obtained:

$$E_{(t)} = \sum_{i=1}^{i=n} E_i e^{-t/\tau_i} \quad (5)$$

where σ = stress, τ = relaxation time constant and E = elastic modulus; subscripts: 0 = start of relaxation, i = i th Maxwell unit and n = number of Maxwell units.

However, even if $\Delta t < \tau_n$, it is necessary to take into account the relaxation phenomena during the stressing period. Many approximation methods have been proposed and one of the simplest is the Zappas approximation which has been used, among others, by Comby *et al.* (1985):

$$E_{(t - \Delta t/2)} = \sigma_{(t)}/\varepsilon \quad (6)$$

Relaxation experiments in which most of the original stress is allowed to relax can, in practice, never be adequately represented by a single relaxation process. Nevertheless, such an approximation may be useful for practical applications, for example in evaluating the springiness of gels (Windwood *et al.*, 1985). When a second relaxation time is added, a much better fitting of

the experimental curves is obtained (see, for example, Costell *et al.*, 1985). In practice, two relaxation times are frequently considered as sufficient (Gross *et al.*, 1980; Comby *et al.*, 1985). Most often graphical or computerised methods based on Inokuchi's technique of successive residuals (Sherman, 1970) are used (Comby *et al.*, 1985; Costell *et al.*, 1985). Non-linear regression analysis by computer is sometimes used (Gross *et al.*, 1980) but, from the authors' own experience, fitting the whole curve in a single step gives erroneous results. In any case, it is difficult to calculate a third relaxation time with sufficient precision and a fourth will generally have no meaning. The longest relaxation time, which is determined first (τ_1), is known with greater accuracy than the next longest. However, it is not possible to ascertain that a longer τ and a different value of E would not have been obtained if the relaxation curve had been observed for a longer period of time. If it was really the case, the other (shorter) relaxation times and the corresponding values of E would be changed accordingly. Peleg and Pollak (1982) have used this argument to claim that the close fit of relaxation curves with two or three exponential terms decaying to zero is a mathematical artefact. On the other hand, as the duration, Δt , of the stressing phase is finite, it is not possible to observe relaxation mechanisms having a characteristic time less than Δt , if they exist. It is frequently observed that the condition $\Delta t \ll \tau_1$ is not obeyed and, therefore, the value of E_1 is underestimated (see, for instance, Costell *et al.*, 1985). In many cases the published experimental information may be insufficient to answer the question (Gross *et al.*, 1980).

Frequently, it is not checked whether the measurements have been made in the linear range where $E(t)$ (eqn. (5)) is independent on the strain ϵ . In most cases, this requirement would not be met and the values calculated for E_i and τ_i would be a function of ϵ . However, at low values of ϵ and if the stressing curve $\sigma(\epsilon)$ is a straight line, the linear approximation may be considered as acceptable (Comby *et al.*, 1985). Comby *et al.*'s experimental results on cylindrical samples of pectin gel (compression rate 0.2 cm min^{-1} , $\epsilon = 0.018$) have been used by the authors to compare the Young's modulus E_0 calculated from the slope of $\sigma(\epsilon)$ with $(E_1 + E_2)$ obtained from the relaxation curves. Both values have similar magnitudes but the latter underestimates E_0 by about 15% (see Fig. 2). Examination of plots of $\log E(t - t/2)$ (eqn. (6)) versus $\log t$ shows inflection points which can be attributed to the pseudo-elastic plateau moduli E_p . This value correlates well with E_0 (see Fig. 3) but is underestimated by approximately 10% as compared with E_0 . This discrepancy may be tentatively attributed to the fact that the gel has been considered as a viscoelastic liquid: if it was a

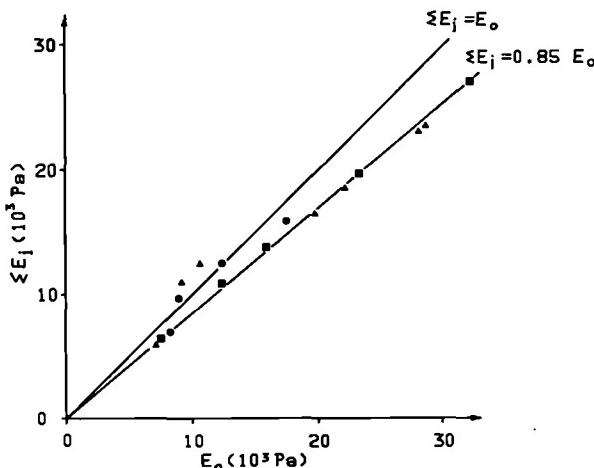


Fig. 2. Relationship between elastic moduli derived from relaxation curves and apparent Young's moduli (E_0). Pectin gel samples, with the following variables: pectin concentration (1.4–1.8%, ●), pH (2.4–3.2, ▲) and sucrose concentration (50–72%, ■) (from Comby *et al.*, 1985).

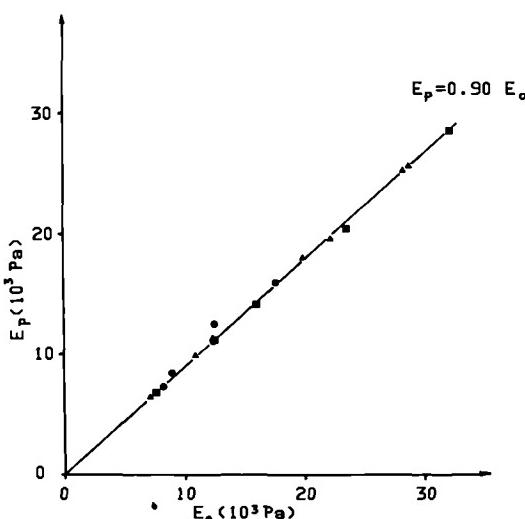


Fig. 3. Relationship between elastic plateau moduli determined on relaxation curves and apparent Young's moduli (E_0) (see Fig. 2) (from Comby *et al.*, 1985).

viscoelastic solid the stress would not decay to zero but, after a sufficiently long time, to an equilibrium stress σ_∞ , corresponding to a long-term equilibrium modulus $E_\infty (= \sigma_\infty/\varepsilon)$. In that case, σ has to be replaced in eqns. (1), (2) and (4) by $(\sigma - \sigma_\infty)$ and, in eqns. (3) and (5), $E_{(t)}$ by $(E_{(t)} - E_\infty)$. In an analogue model, this Hookean spring (E_∞) would be put in parallel with the Maxwellian units (see Fig. 1c). However, with biological materials it is very difficult to decide if the stress decays to zero or not because lengthy experiments would encounter changes in their physical and biochemical properties (Peleg and Pollak, 1982). Another hypothesis could be that a small but significant part of the compression force is used to overcome friction at the interface between the gel surface and the testing equipment, thus leading to a slight overestimate of E_0 . In addition, it cannot be ascertained solely on the basis of these published data that the behaviour is strictly linear. However, the consistency of the Young's moduli values estimated by these different methods can be considered, as a first approximation, as satisfactory.

A discrete representation of several relaxation times may be replaced by a continuous spectrum when eqn. (5) becomes (Ferry, 1980)

$$E_{(t)} = \int_{-\infty}^{+\infty} H(\tau) e^{-t/\tau} d \ln \tau \quad (7)$$

where $H(\tau)$ is the distribution function of relaxation times. This approach is the most straightforward but, generally, does not permit the description of the relaxation curve in a simple analytical form.

3. NON-LINEAR BEHAVIOUR

In most publications concerning food materials, the use of exponential decay terms to describe experimental relaxation curves is no more than a mathematical fitting process, because the behaviour is not linear. This may be due to the applied strain level, even if fairly small, being in most cases out of the linear viscoelastic domain. The resulting properties will depend, in particular, on strain and strain rate. Peleg (1984) has recently discussed how to select a model to represent non-linear behaviour. Among others, two methods may be followed using elastic and viscous elements with non-linear properties, or using a variable number of linear elements. In the latter case, fracture and/or contact elements inactivating or activating linear elements are introduced into the model (Peleg, 1984; Miller *et al.*, 1986). However, it is generally impossible to select from among various options on

a theoretical basis and several equations may have similar fitting capabilities.

One of the simplest methods of fitting experimental relaxation curves for solid biological materials has been proposed by Peleg (1979, 1980). He has shown that the stress (or force) decay may be linearised in the form

$$t\sigma_0/(\sigma_0 - \sigma) = k_1 + k_2 t \quad (8)$$

When times are long, it is easy to show that

$$\sigma \rightarrow \sigma_\infty = \sigma_0(k_2 - 1)/k_2 \quad (9)$$

If $k_2 = 1$, the stress relaxes completely and the material behaves as a viscoelastic liquid. In most cases $k_2 > 1$, implying a solid viscoelastic behaviour (Peleg and Normand, 1983):

$$E_\infty = \sigma_0(k_2 - 1)/k_2 \varepsilon \quad (10)$$

Peleg and Pollak (1982) consider that the values of E_∞ are hypothetical, even if they have a practical interest, because biological materials are unstable and do not reach true mechanical equilibrium. In addition, the statement that E_∞ is a function of the initial stress σ_0 is questionable.

From eqn. (8),

$$d\sigma/dt = -k_1 \sigma_0/(k_1 + k_2 t)^2 \quad (11)$$

when $t \rightarrow 0$, $d\sigma/dt \rightarrow \sigma_0/k_1$. Therefore, in the vicinity of $t=0$, Peleg's equation is equivalent to a Maxwell model with $\tau = k_1$. Equation (8) has been applied to various solid food materials (Peleg, 1979, 1980; Peleg and Normand, 1983), to pectin gels (Peleg, 1980), to agar gels (Peleg, 1979; Costell *et al.*, 1985; Windwood *et al.*, 1985), and to kappa carrageenan, alginate and carrageenan/locust bean gum gels (Windwood *et al.*, 1985). The last-named authors have shown that k_1 and k_2 decrease with the degree of compression. The decrease in k_2 has been interpreted as an early indication of failure (Peleg, 1980; Pollak and Peleg, 1980). The stress relaxation pattern for powders has also been described by eqn. (8) (Moreyra and Peleg, 1980).

Peleg and Normand (1983) have compared eqns. (4) and (8) for evaluating stress-relaxation results for solid foods. They have used published exponential relaxation equations to generate data. They concluded that the fit given by eqn. (8) was excellent for equations containing at least three exponential decay terms. The fit was not as good for some of the two-term exponential equations. This could be due to the lack of an accurate description of the initial stage of the relaxation process with only two decay

terms. However, as a direct comparison with experimental values was not possible, the conclusions have to be regarded with caution.

Experimental evidence indicates that, at sufficiently long times, the relaxation process often obeys a power law:

$$\frac{d\sigma}{dt} = -A\sigma^m \quad (12)$$

For a viscoelastic solid; σ has to be replaced by $(\sigma - \sigma_\infty)$. Among others, Inda and Rha (1982) have found that eqn. (12) may be used to describe the tensile stress relaxation of gluten.

A very simple equation has been proposed (Launay, 1979) to describe shear stress relaxation in wheat flour doughs. It is based on a non-linear Lethersich model (Fig. 1b) in which the viscous properties obey a power law and the shear modulus is a function of the elastic deformation of the spring. However, if this modulus is constant during the relaxation process, eqn. (13) is obtained:

$$\log(\sigma/\sigma_0) = -\log[1 + K(n-1)t]/(n-1) \quad (13)$$

where $1/n$ is the power-law exponent for viscous flow.

Equation (13) has also been applied to stress relaxation after biaxial extension of dough with the Chopin Alveograph (Launay, in press). A very good fit with the experimental curves is observed in both cases. When $K(n-1)t \gg 1$, eqn. (12) is obeyed. At the beginning of the relaxation process, when $K(n-1)t \ll 1$, eqn. (13) corresponds to an exponential decay of the stress with a relaxation time $\tau = 1/K$. Therefore, at short and long times, eqn. (13) takes meaningful limiting forms.

If the non-linear viscoelastic behaviour of a solid is to be described, the model of Fig. 1c may be used and eqn. (14) is obtained:

$$\log(\sigma - \sigma_\infty)/(\sigma_0 - \sigma_\infty) = -\log[1 + K(n-1)t]/(n-1) \quad (14)$$

The authors have compared eqns. (8) and (14) for their ability to fit relaxation data obtained with three food products: apple (Golden Delicious) and potato (Ostara) flesh, and processed cheese (mini Babybel). Cylindrical test samples were prepared with a device similar to a cork borer and then cut to the required length with a razor blade. Samples have to be trimmed very slowly in order to obtain the correct dimensions, and this is particularly important for 'rubbery' materials. The cylinders were compressed between a PVC piston and the metal plate of an Instron (model 1121) interfaced with an HP 87 microcomputer. During measurement samples were in contact with the laboratory atmosphere (temperature 25°C, relative humidity 30%, approximately). Maximum compression

$\Delta h/h_0$ was fixed at 5% when it was possible, as a first approximation, to use the Cauchy definition of strain ($\epsilon = \Delta h/h_0$) and to disregard section and shape changes. Compression rates were rather low (0.5, 1 and 2 cm min⁻¹) so as to collect numerous experimental values at the beginning of relaxation. A computer program in Basic was written in order to:

- (a) Compress the sample at a given cross-head speed, thereby achieving a particular Cauchy strain.
- (b) Store data points during compression and relaxation at predetermined sampling frequencies.
- (c) Define precisely the beginning of the relaxation curve ($t = 0; F = F_0$) as the intersection point of the regression lines ($t; F$) calculated from the last three points of the compression cycle and the first three of the relaxation cycle. This method gives a value for F_0 very close to the first sampled in relaxation and provides an accurate estimate of $t = 0$, which is essential because the initial part of the relaxation process is very fast.
- (d) Calculate an apparent Young's modulus from the slope of the regression line corresponding to the second half of the compression curve.

The following information is entered before starting the test: cylinder height and diameter, maximum strain, cross-head speed and sampling frequencies. In this work these were fixed as follows: (i) in compression, every 0.3 s from 0 to 60% of maximum strain and every 0.08 s afterwards; (ii) in relaxation, every 0.08, 2, 20 and 40 s during the periods 0–2, 2–20, 20–240 and 240–360 s, respectively. In many cases it was observed that the slope $|dF/dt|$ increased at the end of relaxation curves. This phenomenon is not consistent with a viscoelastic relaxation process which implies a steady decrease in slope and it may be attributed to instrumental artefacts (slip at contact surfaces) or to slow modifications in sample properties (change in shape, loss of liquid and/or of gas by internal pressure effects, propagation of microcracks...). Therefore, the curves have been analysed by limiting the time scale to 165 s. Equations (8), (13) and (14), written for comparison purposes in the form $F = f(t)$, were fitted to experimental relaxation curves by a computer program (Simplex). Two terms were calculated from eqns. (8) (k_1, k_2) and (13) ($n, (n - 1)K$) and three from eqn. (14) ($n, (n - 1)K, F_\infty$), where F_∞ is the (hypothetical) unrelaxed force at equilibrium. A very low (10^{-5}) standard deviation between experimental and fitted curves was selected as convergence criterion and it was met, except in two cases with eqn. (14), in about 10–40 iterations. The quality of fit may be estimated by the sum of

TABLE 1
QUANTITIES DERIVED FROM UNIAXIAL COMPRESSION AND RELAXATION CURVES:
COMPARISON BETWEEN THE POWER LAW AND PELEG'S EQUATION
(the first line and the second line correspond to unreduced and reduced data sampling, respectively)

Samples	$V^{(1)}$ (cm min^{-1})	$E_{\text{app}}^{(2)}$ (10^6 Pa)	$F_0^{(3)}$ (N)	$F_e^{(4)}$ (N)	Equation (13)					Equation (8)						
					K (s^{-1})	n	% ⁽⁵⁾	$\Sigma^{(6)}$	k_1 (s)	k_2	F_x (N)	E_x (10^6 Pa)	% ⁽⁵⁾	$\Sigma^{(6)}$		
Apple 1	0.5	1.54	15.7	10.7	0.053	14.6		$\times 10^4$	35.1	3.37	11.0	0.97	3.2	3.8		
					0.038	12.8	4.2	0.21		47.8	3.11	10.7	0.94	4.5	0.96	
Apple 2	1	1.92	20.3	13.3	0.096	14.3	7.5	1.4	19.0	3.22	14.0	1.23	7.3	9.9		
					0.070	12.8	4.5	0.33		31.4	2.86	13.2	1.16	9.7	2.3	
Apple 2	2	2.02	20.7	20.7	0.147	15.1	9.8	1.0	12.4	3.27	14.4	1.27	5.0	11.1		
					0.107	13.7	5.7	0.34		23.1	2.89	13.5	1.19	4.5	3.1	
Potato	0.5	1.03	8.9	6.2	0.180	19.7		$\times 10^4$	10.8	3.96	6.65	0.59	5.1	1.6		
					0.133	18.1	0.73	0.047		22.4	3.47	6.34	0.56	9.5	0.51	
	1	2.54	22.2	16.7	0.147	24.7	5.0	0.71	13.8	4.84	17.6	1.55	0.73	7.6		
					0.105	22.3	5.4	0.32		29.0	4.23	23.3	1.50	4.4	2.5	
	2	3.26	29.6	21.9	0.296	26.3	9.9	1.0	8.47	4.72	17.0	2.05	5.9	14.2		
					0.218	24.4	5.9	0.44		17.9	4.18	22.5	1.98	8.7	5.2	
Cheese 1	0.5	0.033	0.45	0.145	0.120	5.4		$\times 10^6$	6.7	0.27	13.1	1.56	0.162	0.014	$\times 10^6$	$\times 10^2$
					0.088	4.7	6.2	0.048		17.8	1.45	0.140	0.012	2.7	0.22	
2	1	0.031	0.45	0.106	0.193	4.9	3.4	0.37	7.63	1.44	0.138	0.012	6.2	1.6		
					0.136	4.2	9.3	0.11		11.6	1.32	0.109	0.0096	8.0	0.40	
3	1	0.034	0.44	0.125	0.203	5.4	2.1	0.23	7.41	1.54	0.154	0.014	2.7	1.3		
					0.145	4.8	3.9	0.058		11.2	1.42	0.130	0.011	8.0	0.32	
4	2	0.026	0.38	0.090	0.332	5.2	5.6	0.16	4.52	1.47	0.121	0.011	2.9	1.2		
					0.250	4.7	5.8	0.047		7.07	1.34	0.096	0.0085	2.2	0.35	

⁽¹⁾Cross-head speed. ⁽²⁾Apparent Young's modulus. ⁽³⁾Force at $t = 0$ (beginning of the relaxation). ⁽⁴⁾Last experimental value (end of relaxation). ⁽⁵⁾Standard deviation. ⁽⁶⁾Sum of squares of differences between experimental and fitted values.

squared differences (Σ) between experimental and calculated values of F . On this basis, it appears that eqn. (14) does not give in every case a better fit than eqn. (13). Moreover, F_∞ may be negative and F_∞ , or its absolute value, is always much smaller than the last experimental data point, F_e . In addition, the convergence criterion is more rapidly met with eqn. (13) than with eqn. (14). Consequently, assuming $F_\infty = 0$, eqn. (13) is considered more realistic than eqn. (14) and it has been used in the following analysis.

Results are given in Table 1. In every case, the fit is better with eqn. (13) than with eqn. (8) if Σ values are compared. k_2 (eqn. (8)) is >1 , even for the cheese sample. Equation (15), derived from eqn. (10), gives the value of the force at equilibrium, F_∞ :

$$F_\infty = F_0(k_2 - 1)/k_2 \quad (15)$$

This result is at variance with the behaviour predicted by eqn. (13), where $F_\infty = 0$. However, Fig. 4 shows that, for the apple and potato samples, F_∞ is closely related to F_e : $F_\infty = 1.06F_e$. For the cheese sample, $F_\infty > F_e$ is also observed. This renders F_∞ meaningless, at least for evaluating equilibrium elastic properties, because its value will depend on the duration of relaxation time. Peleg and Pollak (1982) found F_∞ to equal about 80–100% F_e for a range of food products. This was independent of the imposed strain.

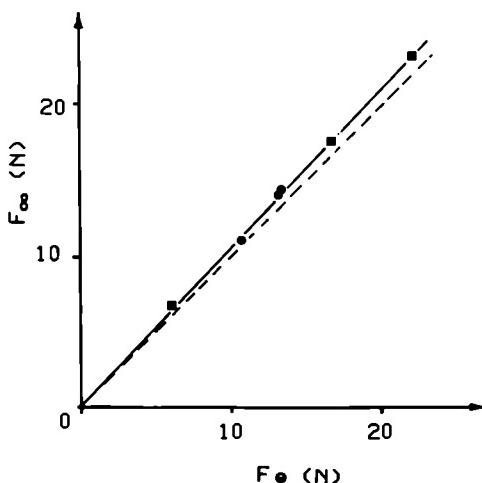


Fig. 4. Regression lines between forces extrapolated to 'infinite' time (F_∞) with Peleg's equation and last experimental values (F_e). Results from Table 1. Continuous line: apple (●) and potato (■) samples; dotted line: $F_\infty = F_e$.

In the present results $F_\infty > F_e$, probably because force versus time was used, instead of its linearised counterpart, as used by Peleg.

In the model developed for wheat flour dough (Launay, *in press*), the quantity $1/n$ is the power-law exponent for pure viscous flow. A very high value of n would mean that the part of the stress attributed to internal viscosity will become almost independent of strain rate; this is a 'solid-like' characteristic. In this respect, the comparison of the values of n for the three food samples is clearly indicative of their contrasting rheological behaviour. In addition, n is almost independent of strain rate for the cheese and apple samples.

In many publications, the results used to analyse the behaviour are those which can be read on a potentiometric recorder and data sampling frequency is rather slow. If less weight is given to the initial part of the relaxation curve, the calculated relaxation rates K and k_1^{-1} will be slower. Table 1 shows that K is about 25% less; exponent n is also 8% less. However, when compared to eqn. (8), the fitting ability of eqn. (13) is also much better, as can be seen in Table 1 and Fig. 5. It may be noted that F_∞ calculated from Peleg's equation is greater than F_e in most cases.

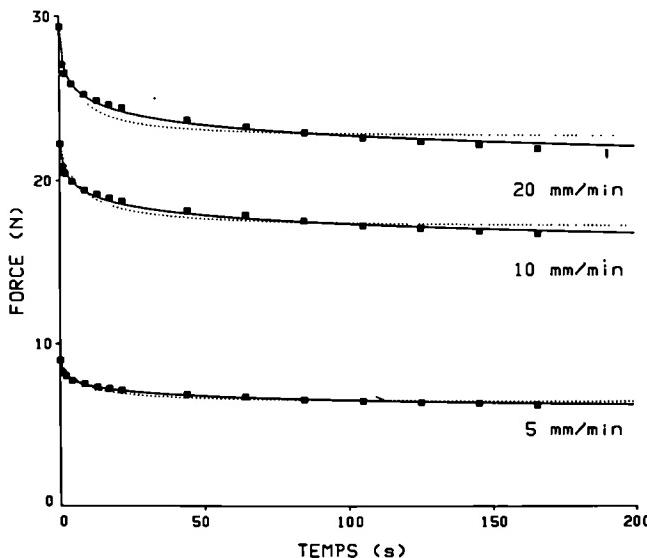


Fig. 5. Comparison between experimental relaxation data (■) and computer-fitted curves with eqns. (8) (dotted line) and (13) (continuous line). Potato flesh, cross-head speed as indicated, reduced data sampling (see text).

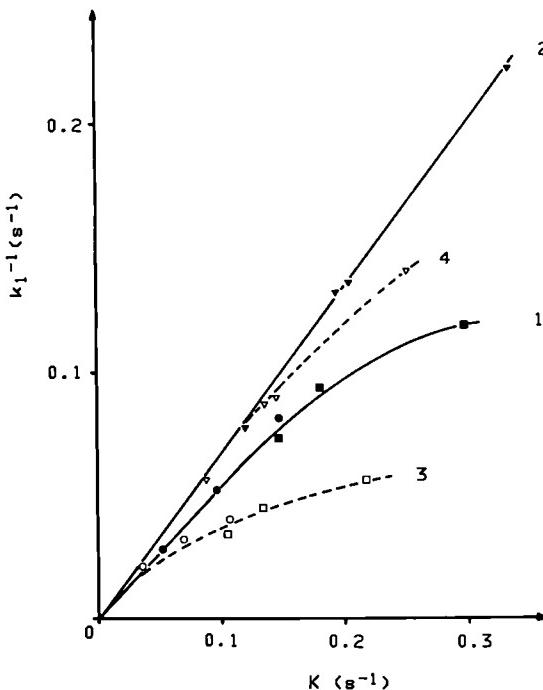


Fig. 6. Relationship between the rate constant K in eqn. (13) and the reciprocal of the characteristic time k_1 in eqn. (8). Apple (\bullet , \circ), potato (\blacksquare , \square) and cheese (∇ , \triangledown) samples; continuous (1, 2) and interrupted (3, 4) lines for fast and reduced data sampling, respectively.

It has been shown that, at the very beginning of the relaxation process, K and k_1^{-1} should be equivalent to the reciprocal of a Maxwellian relaxation time. Figure 6 shows that k_1^{-1} is consistently less than K , even if these values are of similar magnitude, and the gap increases when the frequency of data sampling decreases. It seems that the same relationship between K and k_1^{-1} holds for the potato and apple samples; it is linear at low relaxation rates and less than linear at higher rates. The relationship is linear for the cheese sample at high data sampling frequency. In both cases, the shape of the curves depends on data sampling frequency beyond a critical relaxation rate. Therefore, great care must be exercised when comparing the relaxation rate behaviour of different foods: the conclusions may be dependent on the selected model and on data sampling frequency.

4. CONCLUSIONS

The applicability of eqn. (13) for describing non-linear stress relaxation in solid food materials has been illustrated. At least on the basis of the results presented here, it fits experimental results much better than does the equation proposed by Peleg, without any extra term. Adding a third term corresponding to the (hypothetical) equilibrium elastic modulus (eqn. (14)) does not bring any benefit and F_∞ , the extrapolated value of the force, is much lower than the last experimental value of F_e , and even negative in some cases. Conversely, Peleg's equation gives F_∞ values always close to but consistently greater than F_e ; they are certainly meaningless in so far as they are intended to predict the long-term rheological behaviour of the sample. Taking into account the unstable properties of biological materials, true mechanical equilibrium will never be reached. In particular, it is not possible to check if the liquid-like behaviour predicted by eqn. (13) is valid or not. Using this equation and the values in Table 1 (rapid data sampling), it may be calculated that for the force to decay to 10% of its initial value for the cheese sample ($v = 0.5 \text{ cm min}^{-1}$) or to 50% for the potato sample ($v = 2 \text{ cm min}^{-1}$) 12.4 h or $1.8 \times 10^{13} \text{ h}$, respectively, would be needed. The exponent n therefore appears to be a good practical index of the solid-like character of a food product. Finally, it is to be emphasised that the fitted terms are dependent on the rate of data sampling. This point deserves further attention.

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DISCUSSION

H. Schubert asked *B. Launay* if sample size affected the results and, as the 'fit' was evidently better for short than for long relaxation times, were the former more meaningful? *Launay* had not had the opportunity to confirm it fully experimentally, but certainly expected sample size to affect results significantly. If fast data sampling is used, then there is a consistent underestimation of the stress by both Powell's and Peleg's equations in the early part of the relaxation period, Powell's appearing worst in those conditions. However, with such complex materials, the duration of the compression stage greatly affected the first part of the relaxation. In the examples presented, the duration of compression ranged from 2 to 20 s and the relaxation from 200 to 400 s. He was accordingly unable to confirm or deny *Schubert's* suggestion from these results. *J. de Baerdemaeker* asked if *Launay* had compared the data fits of Powell and Peleg with that of an exponential equation corresponding to a generalised Maxwell model

(rather than trying to fit experimental points to selected equations!). He also thought that the *information* content of the earlier part of the relaxation curve so much greater than that of the later part that the later part was much less important—except for the asymptote value it provided. *Launay* agreed. He had tried a Maxwell-type fit. Sometimes it worked, sometimes not. He felt that the best fit *was* the objective and that was given by Powell's or Peleg's equations. *de Baerdemaeker* suggested it might be best just to fix the exponential relaxation times at, say, 10, 100 and 1000. *Launay* said that was a quick method which usually required three relaxation times but occasionally two sufficed if determined by iteration—or by shrewd first estimation.

Studies of the Rheological Behaviour of Carrots and Potatoes during Cooking

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1. INTRODUCTION

Thermal treatment is one of the most important processes in the manufacture of storable and ready-to-serve food products of agricultural origin; during thermal treatment, many desirable and undesirable reactions take place; components such as vitamins and colour components, for example, and also physical properties, such as texture, may be changed.

Whereas changes in components have been studied in great detail, relatively little data have been available on changes in texture due to thermal treatment.¹ To explore such changes the influence of heating on tissue firmness in carrots and potatoes—two products of some importance in industrial food processing—were studied by means of an instrumental measuring method.

2. EXPERIMENTAL

Carrots, variety Nantaise, and potatoes, varieties Bintje and Saskia, were investigated. For this purpose, cylinders, diameter $D = 30$ mm, were bored from the carrots and potatoes and cut into slices, thickness $d = 3$ mm (Fig. 1).

The slices were treated thermally by immersion in a waterbath. Experimental variables were water temperature ($70^\circ\text{C} \leq T \leq 100^\circ\text{C}$), immersion time ($0\text{ min} \leq t \leq 30\text{ min}$), and, in the case of carrots, pH of the water ($3 \leq \text{pH} \leq 12.5$) and its Ca^{2+} concentration (0 M and 0.1 M). Demineralised water was used in all experiments.

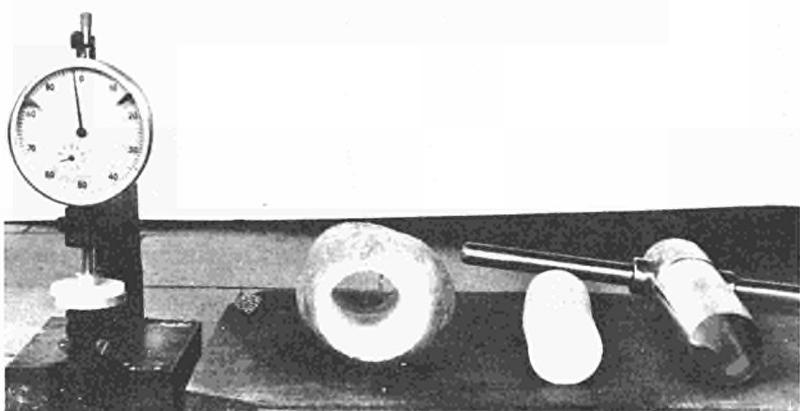


Fig. 1. Sample preparation.

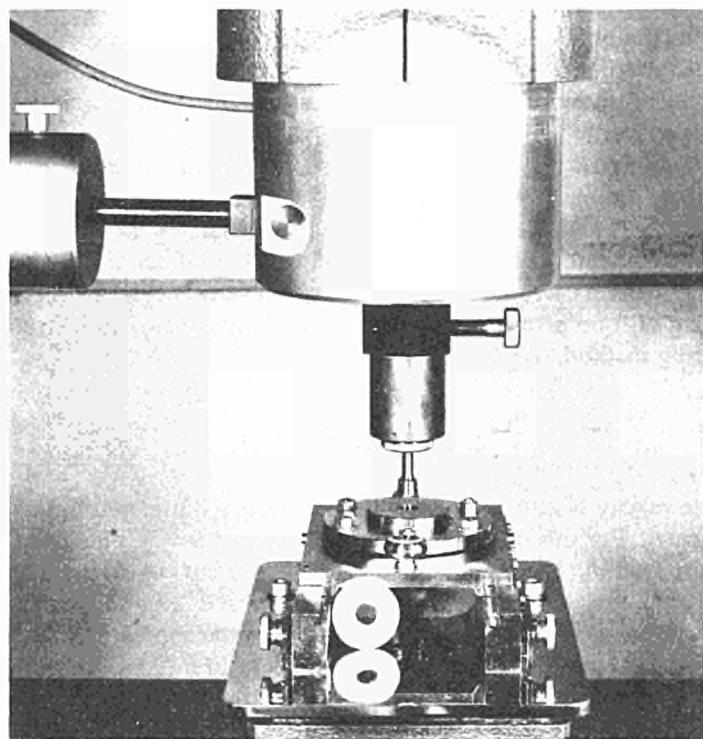


Fig. 2. Measurement of shear strength.

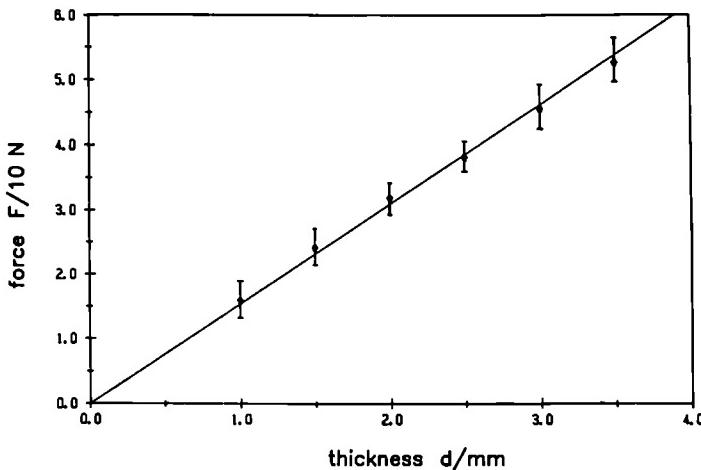


Fig. 3. Maximum shear force as function of thickness of raw potato slices (variety: Bintje).

Tissue firmness was determined by measurement of the shear strength on universal testing machines (Instron 1140 and Zwick 1442). The maximum force during the shearing process was recorded as the characteristic measurement (Figs. 2 and 3).

3. RESULTS AND DISCUSSION

Firmness of the Raw Material

Compilation of the measured values of more than 600 individual measurements showed distributions which were skewed to the left; the tissue of carrots exhibited greater shear strength than that of potatoes (Figs. 4 and 5, Table 1).

TABLE 1
SHEAR STRENGTH (MAX. SHEAR FORCE F) OF RAW
CARROTS AND POTATOES

Material	$F(N)$	$s(N)$
Potatoes, Bintje	37.90	3.18
Potatoes, Saskia	31.90	4.90
Carrots, Nantaise	58.69	13.40

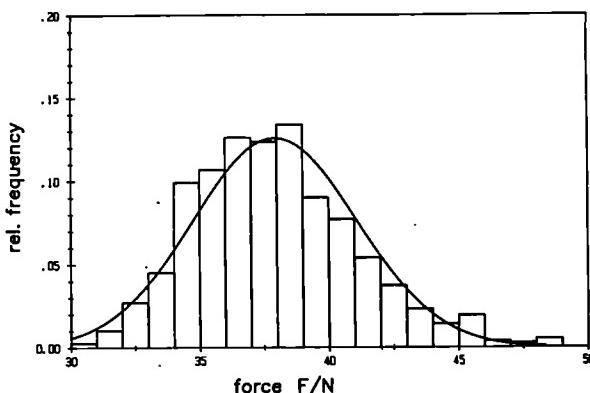


Fig. 4. Shear strength of raw potato slices (variety: Bintje).

Firmness of the Thermally Treated Material

A marked change in tissue firmness is observed after treatment in water only at temperatures of $T > 70^\circ\text{C}$ (Fig. 6).

Microscopic studies of the potato tissue have shown that the starch granules swell first before they gelatinise. Any changes in the middle lamella were not evident microscopically after treatments lasting up to 20 min.

On semi-logarithmic coordinates two stages appear which can be approximated by two straight lines (Figs. 7 and 8).

The decrease in shear strength as found experimentally can be explained by two mechanisms of the type

$$\ln F = \ln F_0 - kt$$

where F = force, F_0 = initial force, k = rate constant and t = time.

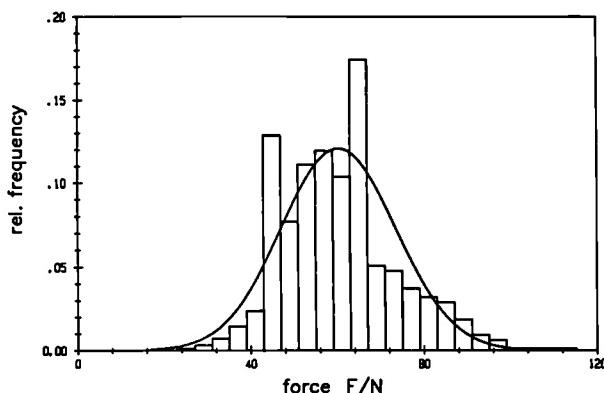


Fig. 5. Shear strength of raw carrot slices (variety: Nantaise).

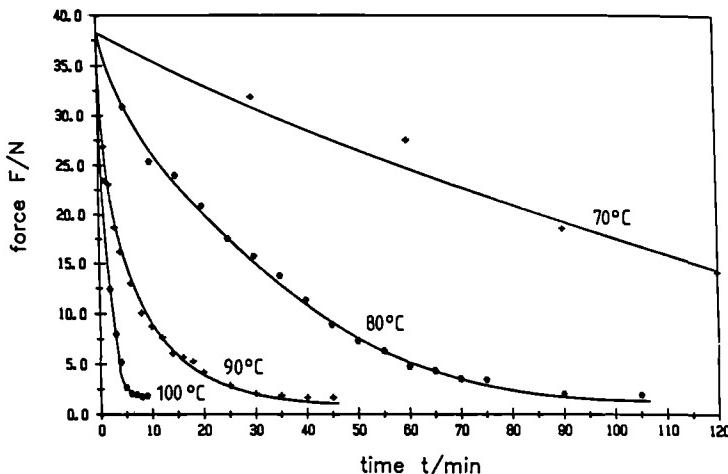


Fig. 6. Shear strength of thermally treated potato slices (variety: Bintje).

Combining the results obtained at different temperatures, this equation can be extended to

$$\ln F = \ln F_0 - k_* \exp(-E_a/RT)t$$

where k_* = rate constant, E_a = activation energy, R = gas constant and T = temperature.

It is therefore assumed that shear strength decreases according to two first-order reactions. Trials with other reaction-kinetic approaches (zeroth,

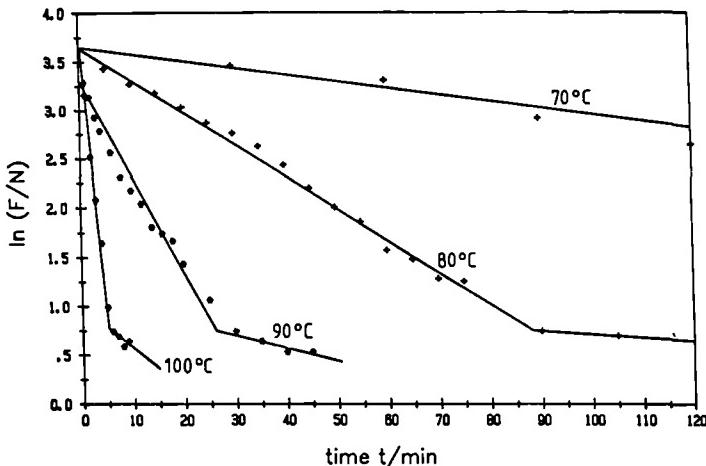


Fig. 7. Shear strength of thermally treated potato slices (variety: Bintje).

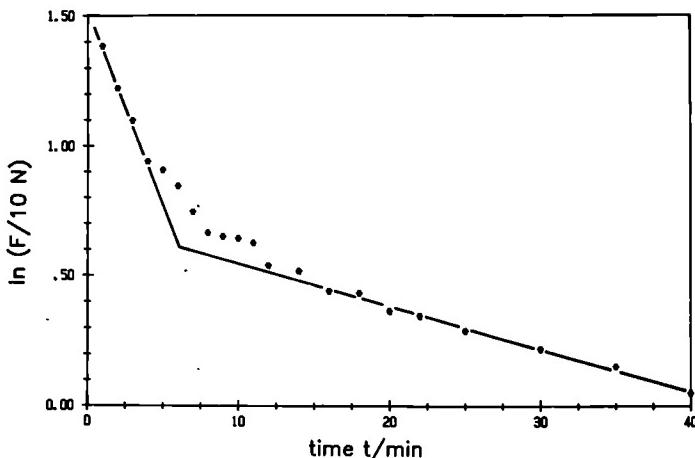


Fig. 8. Shear strength of thermally treated carrot slices ($T = 95^\circ\text{C}$; pH 7).

1.5th and 2nd order) confirmed that the selected approach describes the measuring results best (Fig. 9, Table 2).

Experimental results with potato slices at different pH values, increased Ca^{2+} concentration at a constant temperature of 84°C have shown that at high pH values tissue firmness decreases very rapidly until complete breakdown of the cellular components after only a few minutes, whereas at low pH values and elevated Ca^{2+} concentration, the decrease in tissue firmness is very slow. All measurements obtained at high pH may be allocated to the first section, and those at low pH to the second section of the curve describing the decrease in tissue firmness at pH 7 (Figs. 10 and 11).

The sum total of all the observations on the decrease in shear strength of carrots and potatoes leads to the conclusion that the distinct reduction

TABLE 2
APPARENT ACTIVATION ENERGY E_a FOR THE DECREASE IN SHEAR
STRENGTH OF THERMALLY TREATED CARROTS AND POTATOES

Material	1st section	2nd section
Potatoes (Bintje)	$146.7 \text{ kJ mol}^{-1}$ ($\ln k_* = 46.51$)	
Potatoes (Saskia)	$119.1 \text{ kJ mol}^{-1}$ ($\ln k_* = 36.86$)	
Carrots (Nantaise)	$143.0 \text{ kJ mol}^{-1}$ ($\ln k_* = 44.70$)	1155 kJ mol^{-1} ($\ln k_* = 33.60$)

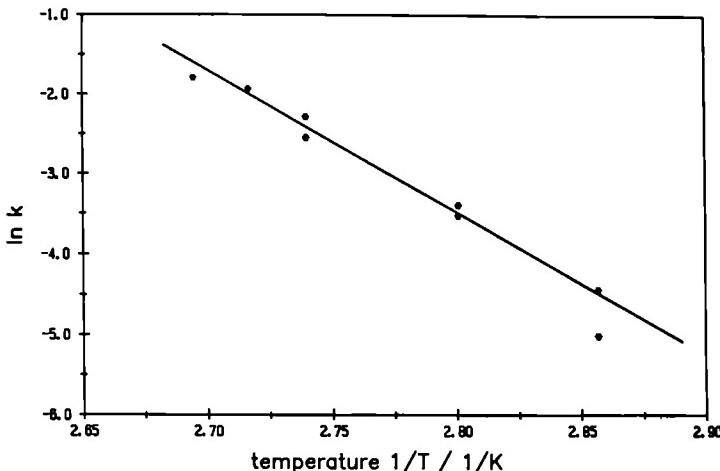


Fig. 9. Reaction rate of the decrease in shear strength during thermal treatment of carrots.

initially is due to splitting of the pectin of the middle lamellae. This changed pectin is water-soluble and loses its cementing function. Loosening of the cell contents and decrease in shear strength of the tissue are the result. Along with the degradation of the pectin of the middle lamella, the pectin of the cell walls (primary wall) also changes, but much more slowly, since the pectin of cell walls is much more stable, or less reactive.

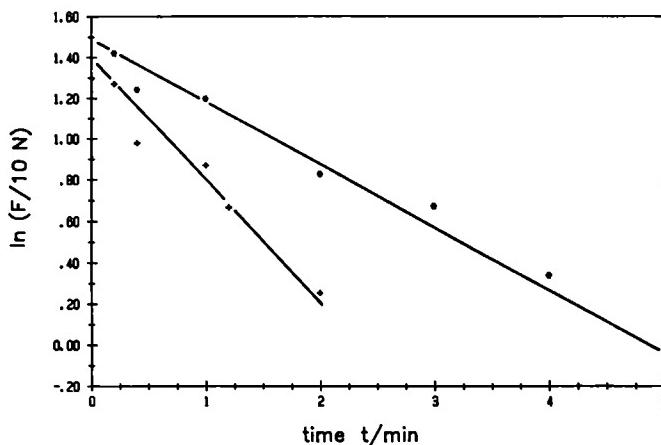


Fig. 10. Shear strength of thermally treated carrot slices (variety: Nantaise). ($T = 84^\circ\text{C}$; * = pH 8; + = pH 12.5).

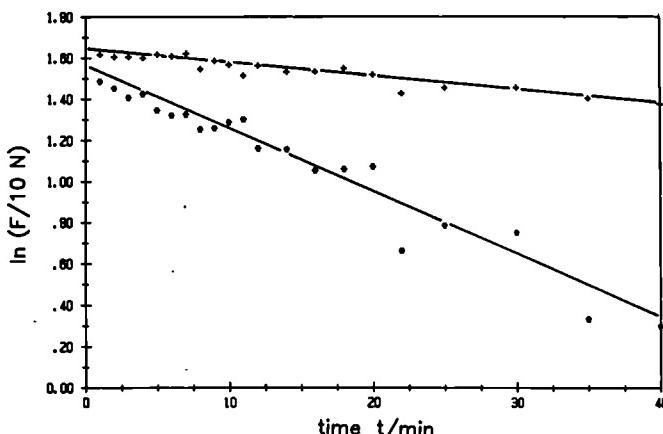


Fig. 11. Shear strength of thermally treated carrot slices (variety: Nantaise). ($T = 84^\circ\text{C}$; * = pH 3; + = pH 7; 0.1 M CaCl_2).

The experiments with Ca^{2+} ions have shown that it is possible to delay the decrease in tissue firmness during thermal treatment. After extended exposure to heat (cooking), tissue strength decreases even when calcium salts were present.

The data for the present study were generated by R. Gail, Th. Walther and I. Hollstein as part of their thesis submitted for diploma to the Department of Food Technology, University of Hohenheim.

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A Compression Test for Measuring the Gel-forming Ability of Fish Protein

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A comminuted fish product when cooked is a gel-like material with viscoelastic behaviour. Depending on test conditions, different properties of the material dominate. The gel can appear as either linear or non-linear viscoelastic at high and low rates of compression respectively, because of stress relaxation.

Young's modulus of elasticity is indeterminate for large deformations, but calculation of an apparent modulus is possible from the linear part of the stress-strain curve. This modulus and yield stress depend on test conditions, viz. sample dimension, compression rate and test temperature. By choosing test conditions where these effects are minimised information useful for characterising the gel can be read from the stress-strain curve.

SAMPLE PREPARATION

Comminuted fillets of cod were mixed with salt (2%), starch (1.9%), milkpowder (5.25%) and flour (3%). Different dry matter contents were obtained by addition of varying amounts of ice. The ratio of fish dry matter to other dry matter was kept constant. The fish paste was heated for 30 min in a 90°C waterbath, then cooled in ice-water and held at 0°C for 24 h.

From each batch, 6–10 cylindrical samples were cut and kept on ice until testing.

TESTS

An Instron Universal Testing Machine was used for uniaxial compression testing between parallel plates. The platens were much larger in area than the sample.

Four properties were deduced from the compression curve (Fig. 1):

Yield stress

Initial slope of the compression curve (α_1).

Later slope of the compression curve (α_2).

Yield strain.

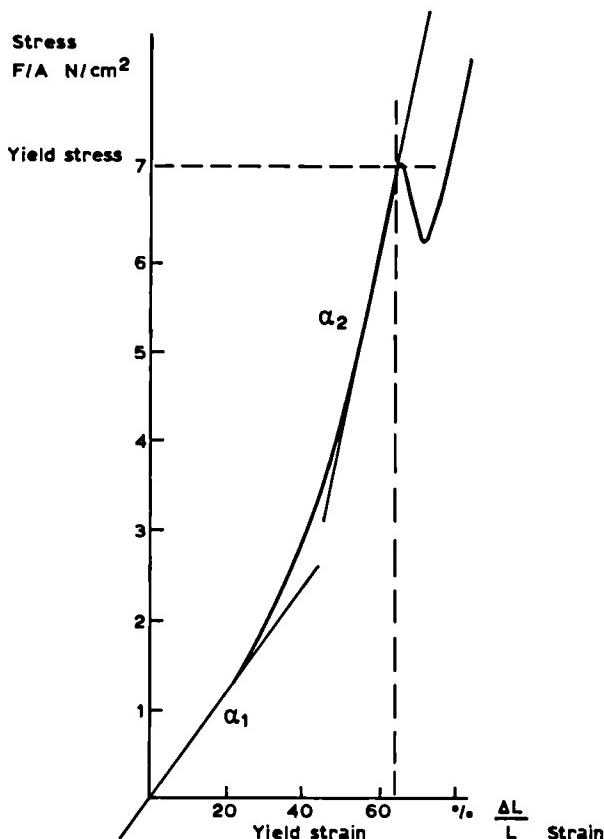


Fig. 1. Compression curve obtained for a sample made from fresh cod.

Yield stress was defined as the force obtained at the point where the curve deviates from the linear ascending part of the curve and divided by the area of the unstrained sample.

An apparent modulus of elasticity was calculated from the slopes of the compression curve at the linear parts of the curve, i.e. initially (α_1) and shortly before the breaking point (α_2).

RESULTS

Examples of results obtained are shown in Figs. 2, 3, 4 and 5, which show, respectively, the effect of sample dimension, rate of compression and test temperature, Figs. 3 and 5 also showing the influence of % dry matter in the samples.

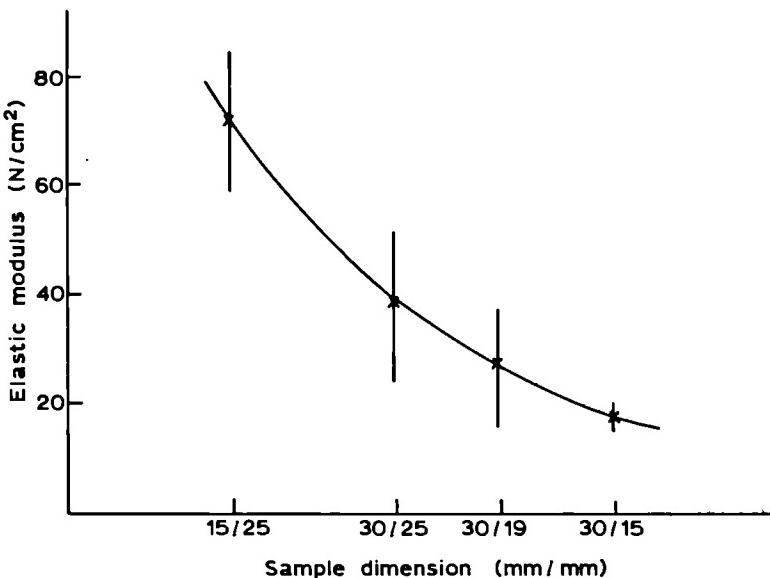


Fig. 2. Late slope of the compression curve as a function of sample height/diameter. The samples were made from fresh fish, salt and ice. Dry matter content 16·0%. Rate of compression 185 mm min⁻¹.

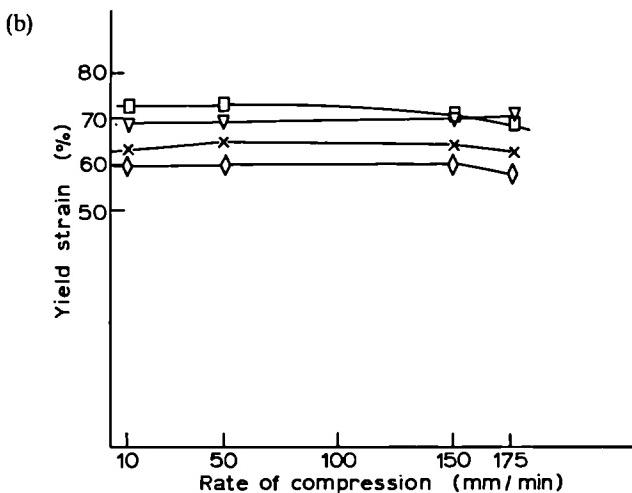
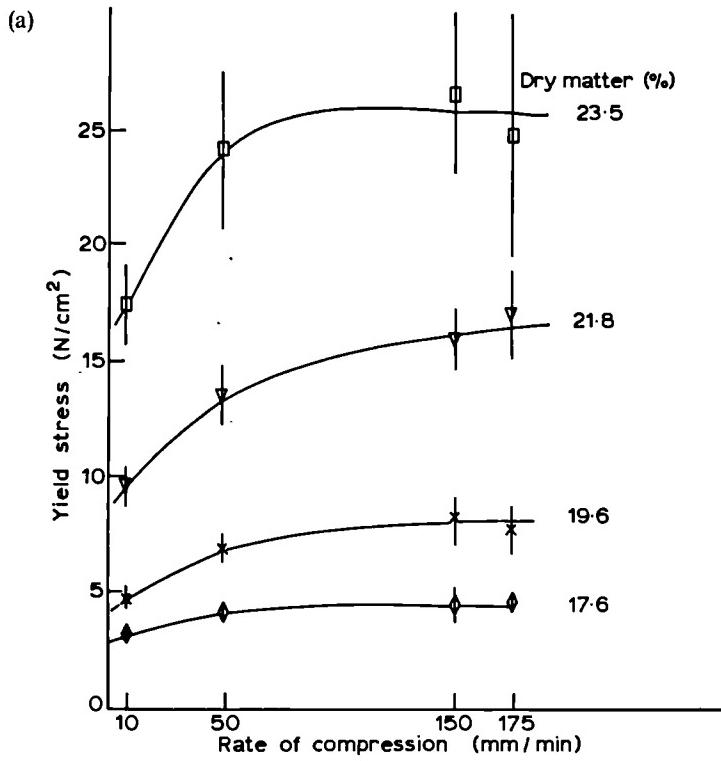


Fig. 3. The dependence of yield stress (a) and yield strain (b) on rate of compression and dry matter percentage. Fresh fish was used. Sample height/diameter 15 mm/15 mm.

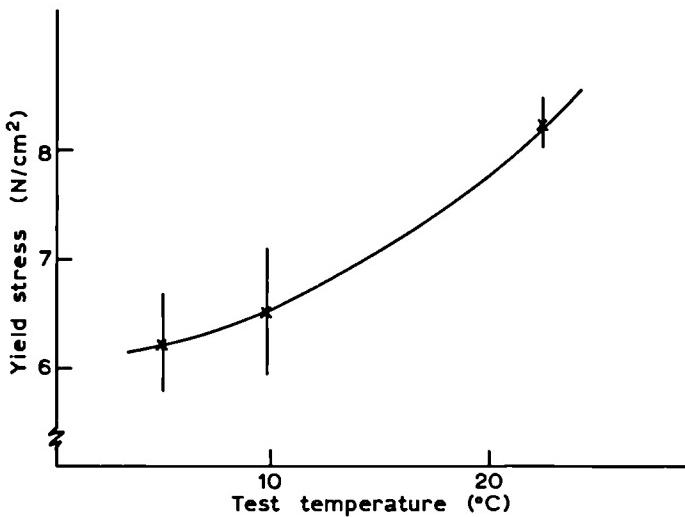


Fig. 4. Influence of sample temperature during test on yield stress value. Sample height/diameter 15 mm/25 mm. Rate of compression 50 mm min⁻¹. Dry matter content 19.4%.

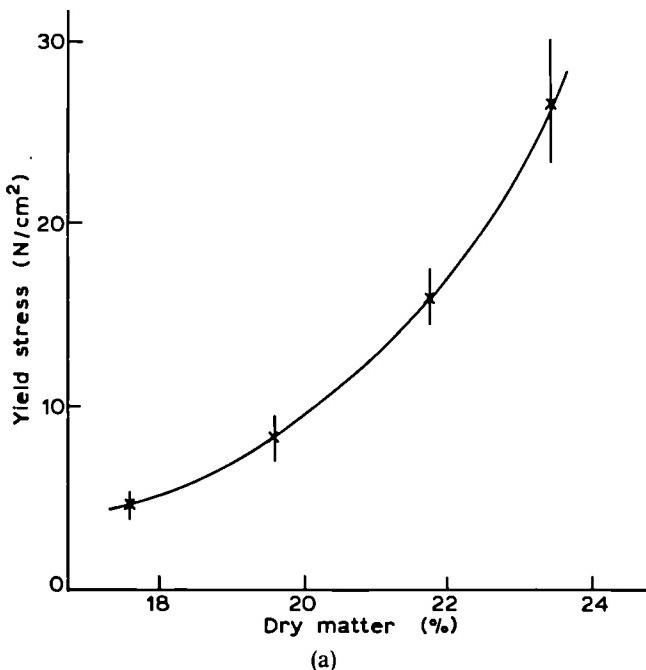
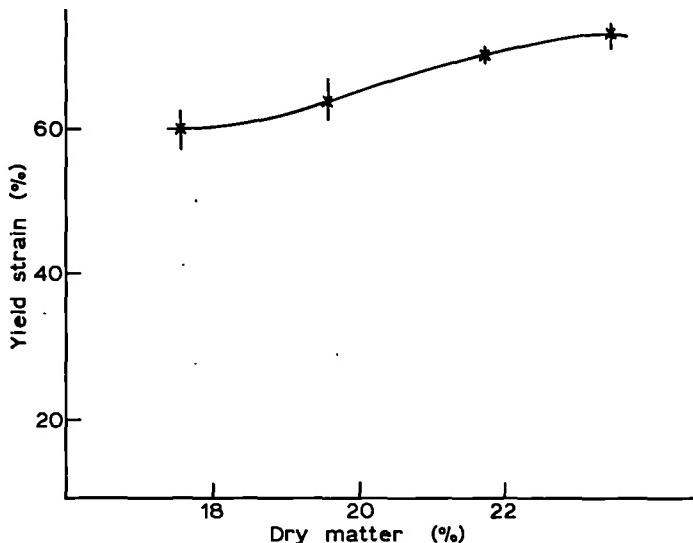


Fig. 5. The dependence of yield stress (a) and yield strain (b) on dry matter percentage. Fresh fish was used. Sample height/diameter 15 mm/15 mm.



(b)
Fig. 5.—contd.

Part 5

DATA COLLECTION

Physical Property Data for Foods: The Contribution of COST 90bis

RONALD JOWITT
COST 90bis Project Leader

INTRODUCTION

COST 90bis was organised in a similar way to COST 90, with a subgroup to deal with each of the three subject areas, but with an additional small group to organise the collection and management of the data as distinct from their *generation*. As it was anticipated that the principal sources of data would be the three subject subgroups, the Data Subgroup was not convened until later in the life of the Project when data were more likely to be available. It included in its membership the chairmen of the three subject subgroups with the Project Leader as its Chairman and Kate Thomas (later Mrs Parkin), a Research Assistant funded by the UK Ministry of Agriculture, Fisheries and Food (MAFF), as its Technical Secretary, from September 1984 to November 1985. The Data Subgroup met twice, its work being carried out mainly by correspondence, or by its members individually or jointly, or under the aegis of the corresponding subject subgroup.

BIBLIOGRAPHIES

Notwithstanding the doubts which have been expressed—often with good cause—regarding the value to other users of published data on physical properties of foods (ppfs), it would be negligent in a Project such as this not to attempt to collect and abstract the published literature on the subject, and this was regarded as a major objective.

Sorption Properties

A bibliography of some 2201 references on sorption isotherms and water activity of foods was published in 1985 (Wolf *et al.*) within the framework of

the Project. The references in it were classified under the headings General and Review; Thermodynamics; Measuring Methods; Influence on Product Stability; References Containing Data—here the references were classified in numerical sequence and also according to foodstuff. The publication was well received by reviewers and, with some support from the Commission, was a commercially viable publication.

Mechanical Properties

A 'first-run' bibliography was obtained by keywords from the MAFF computer reference data base and checked by Kate Thomas. A separate print-out of references was similarly obtained using keywords by Brian McKenna at University College, Dublin, and subsequently found by him to be incomplete, which threw doubt on the adequacy of such computer searches using keywords. He and colleagues at UCD refined the procedure and obtained or consulted those references confirmed as relevant in order to check the content. The references were then collated, assembled into a bibliography and classified in a similar way to that in the Sorption Bibliography. It is intended that the bibliography will be published.

Dielectric and Optical Properties

Private bibliographies and internal data bases were searched using keywords by Mike Kent of the Torry Research Station to produce a bibliography on electrical properties and one on colour of foods. These were circulated to interested participants for checking and supplementing. Both these bibliographies will be published within the COST 90bis framework.

Diffusion Properties

Several members of the Diffusion Subgroup made available to the Data Subgroup their own bibliographies and these were collated and combined by Kate Thomas. One was contributed in completed form by M. Rüegg and W. Schär of the Swiss Federal Dairy Research Institute, Liebefeld/Berne, on Salt Diffusion in Foods, which also contained data extracted from the papers listed in the bibliography. Final collation and classification of the combined diffusion bibliography is the work of André Voilley of Dijon University and D. Vidal of Valencia Polytechnical University with help from the Project Leader. This too will be published (see Chapter 40 by Voilley and Vidal).

There is a need for similar compilations on thermal and liquid properties of foods which will require an input of resources, time and dedication in the

Entry number in bibliography
Author(s)
Title of paper
Complete reference (year of publication, journal, volume number, page numbers, language)

Nature of information contained in this paper

Foods dealt with
Diffusants
Related properties specified
Other contextual information reported
Quantitative data?*
Methodology?
Mathematical relationships?
Review(s) of other papers?
Your assessment of significance #

* If practicable, please attach photocopy(ies).

If outstanding, please attach photocopy.

Fig. 1. COST90bis. Analysis of diffusion bibliography entries.

future, possibly in association with one or more of the European Centres which it is proposed be identified during the period following COST 90bis. An example of a standard form used to characterise references in the bibliographies is reproduced in Fig. 1.

CLASSIFICATION OF FOODS AND PHYSICAL PROPERTIES

The author's Classification, originally published in English and then in English and German, now exists also, unpublished, in French and will shortly exist in Spanish. It is hoped to publish a four-language version within the framework of COST 90bis.

STANDARDISATION OF NOMENCLATURE

A four-language list of definitions, symbols and units for quantities used in relation to ppfs drafted for use within the Project could be included in an appropriate publication of the Project—say the Classification.

PRESENTATION OF INFORMATION

The desirability of standard formats for tables and graphs was considered. Whilst it was felt that good and bad examples of both abound, it was not felt appropriate to propose a standard format since the requirements vary widely with both content and purpose. The present recommendation is that careful thought be given to the objectives, the suitability and the quality of tables and graphs to display ppfs data but that the most appropriate format will be that which best suits the content and purpose in each case. This also applies to the method of presentation of statistical information. Replication or multiplication of measurements in this field is most important and it is essential to include with the results the mean value, the number of values and some recognised measure of the spread of values.

Context

Ppfs data presented without contextual information are unlikely to be of much use. The importance of context to ppfs values is emphasised elsewhere, as is the proposal to study this in the next phase of European ppfs work. In the meantime, until it is known more clearly which contextual

factors do, and which do not, affect the numerical value of a particular property, it is essential to 'contextualise' *as fully as possible* the results of any measurements made and used or published.

CONCLUSIONS

COST 90 made a useful contribution to the quantitative information on ppfs, notably the COSTHERM computer program for calculating the thermal properties of foods from their composition. COST 90bis has added substantially to that contribution, notably by extensive bibliographies on various properties and the extraction of data from the literature cited. The task for the future is to identify particular institutions and individuals in Europe as more permanent custodians of a particular property or group of properties. Such authorities should be supported by committed Community funds for periods of at least 5 years—preferably on a 'rolling' 5 + year commitment basis. In addition, concerted-action-type support for such centres should be organised so that their knowledge base is Europe-wide. Participants would have access to these knowledge/data bases on favourable terms but the information should be readily available at low cost to all who could benefit from it.

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- Rüegg, M. and Schär, W. (1985). *Diffusion of Salt in Food—Bibliography & Data*, Swiss Federal Dairy Research Institute, Liebefeld/Berne.
Wolf, W., Spiess, W. E. L. and Jung, G. (1985). *Sorption Isotherms and Water Activity of Food Materials—a Bibliography*, Science and Technology Publishers, Hornchurch, Essex.

40

Bibliography on Diffusion in Foods

DANIEL VIDAL

*Department of Food Technology,
Polytechnical University of Valencia, Spain*

and

ANDREE VOILLEY

*Laboratory of Physico-Chemical Biology,
ENSBANA, University of Dijon, France*

The aim of this work was to compile as complete a list as possible of publications dealing with diffusion in foods, including the theory, measurement and application of apparent diffusivity, especially those containing diffusion data.

The bibliography was prepared within the COST 90bis project, from references provided by Y. Motarjemi, G. Raouzeos, M. Rüegg, D. Vidal and A. Voilley, from their particular fields of research.

A compilation was made by K. Thomas, with the assistance of the Project Leader R. Jowitt, sorting, collating and combining the considerable bibliographic contributions into a single bibliography of some 550 references.

D. Vidal and A. Voilley, aided by W. E. L. Spiess (papers in German and Japanese), F. Palmia (papers in Italian), D. Ehlermann (papers in Russian) and P. Nesvabda and P. Lewicki (papers in Polish, Czech, Serbo-Croat and Bulgarian) analysed each paper using a form, as exemplified in Fig. 1, and the descriptors indicated in Fig. 2.

Publications in the period 1980–1985 (about 150 references) have already been analysed and the complete analysis of all the references will be published with the bibliography in 1987.

Authors			
Title			
Journal			
Reference			
Year	Language	Number	This should be the serial number of the reference in the bibliography
Content	Review; theory; mathematical model (if the aim); experimental work; methodology		
Food	Foodstuffs (see Ronald Jowitt's Classification of Foodstuffs and Physical Properties; <i>Lebensm. Wiss. u. Technol.</i> , 7(6), 358–371 (1974)) or model systems used in the work		
Food details	Composition; water content; geometry; size; origin; cultivar; (pre)treatments;		
Diffusant(s)	Name of the molecule; macromolecule; electrolyte;		
Diffusants details	Chemical function; ion; concentration;		
Concentration measurement	Method of solute concentration measurement: chemical analysis; gravimetry; chromatography; spectrophotometry; specific electrodes;		
'D' Determination method	Method of apparent diffusivity determination: diaphragm cell; capillary cell (liquids); concentration-distance curves; sorption curves; desorption curves; ESR; NMR; various;		
Contextual information	Factors influencing the diffusion: air flow rate; crystallisation; electrical current; food characteristics (composition, density, dimensions, shape, texture, variety,...); gelatinisation; pH; presence of other substances; pressure; relative humidity; ripening; shrinkage; solute characteristics (concentration, particle size,...); temperature; treatments (blanching, cooking, cutting method, desalting method, drying, freezing, milling, pressing, rewetting, salting method, soaking, stirring, storage, thawing, vibrating,...); treatment duration; viscosity; water activity; water content;		
Data	Apparent diffusivity (table(s), figure(s), value(s), equation(s)); concentration data		

Fig. 1. Format of record made for each reference, with keywords and guide notes.

Authors	Naesens, W.; Bresseleers, G.; Tobback, P.
Title	<i>A method for the determination of diffusion coefficients of food components in low and intermediate moisture systems</i>
Journal	Journal of Food Science
Reference	46(5), 1446-1449
Year	1981 Language English Number 0000
Content	Methodology
Food	Model systems: paraffin oil, microcrystalline cellulose, gum arabic.
Food details	
Diffusant(s)	¹⁴ C labelled tripalmitin and palmitic acid.
Diffusants details	
Concentration measurement	Liquid scintillation counter.
'D' Determination method	Concentration-distance curve: diffusion cylinder.
Contextual information	Water activity (0.33, 0.71)
Data	Apparent diffusivity (table)

Fig. 2. An example of a reference extract record.

The bibliography produced is stored on a 512K Apple Macintosh microcomputer, using Microsoft Corporation Microsoft File Data Base (Version 1.00, December 31, 1984), at the Department of Food Technology, Polytechnic University of Valencia, Spain. Updating and retrieving information is easy, using various types of automatic selection and sort routines.

The USDA NC136 Collaborative Project on Physical and Chemical Properties of Foods

MARTIN R. OKOS

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The need for a compilation of physical and chemical properties of foods for the design and implementation of efficient food processing systems is well recognised by academic and industrial personnel. Unfortunately such data are scattered throughout the literature and it is extremely time-consuming to search through ten to fifteen different sources to locate the necessary data.

For this reason the North Central Research Project 136, which groups certain land-grant universities under the sponsorship of USDA and was formed to coordinate food processing research, undertook to act as a clearinghouse for chemical and physical property data on foods. As the first project, the group decided to review selected physical and chemical properties of foods and present the reviews at the 1983 ASAE winter meeting in Chicago. As a result fourteen review papers were presented.

In order to ensure that papers presented were of high technical quality, complete and accurate, each paper was critically evaluated by several researchers knowledgeable in the field using standards typical of publications refereed for ASAE Transactions. The result is a volume of eleven papers in four main property areas: (a) rheological; (b) thermal; (c) colligative; (d) quality (Okos, 1987).

(a) Rheological

Rheological Properties of Fluid Foods

by J. F. Steffe, I. O. Mohamed and E. W. Ford, Department of Agricultural Engineering, Michigan State University, East Lansing, MI 48823.

Published values for the properties of non-Newtonian fluids are tabulated. Emphasis is placed on inelastic fluids which do not exhibit time-dependent behaviour. A general model proposed by Herschel and Bulkley

is used to describe the flow behaviour of inelastic time-independent fluids. The influence of temperature on flow properties is evaluated by an Arrhenius-type relationship. The paper contains 33 references and 3 tables.

Viscoelastic Properties of Fluid and Semi-solid Foods

by M. A. Rao, Department of Food Science and Technology, New York State Agricultural Experiment Station, Cornell University, Geneva, NY 14456.

Viscoelastic properties of fluid foods are described along with the methods of measurement: normal stress overshoot, oscillatory, creep-compliance and creep-relaxation. Interpretation of results in terms of mechanical models (Newtonian viscosity and an elastic element) has been extensive. Few studies have attempted to relate structure/composition to rheological characteristics. The paper contains 49 references, 8 figures and 4 tables.

(b) Thermal

Thermal Properties of Liquid Foods—Review

by Y. Choi and M. R. Okos, Agricultural Engineering Department, Purdue University, West Lafayette, IN 47907.

Thermal property data and models for liquid foods were reviewed in the literature survey. General mathematical models for predicting the thermal conductivity, thermal diffusivity, density and specific heat of liquid foods based on the corresponding thermal properties of their major pure components were developed to an accuracy of 4.2%. The paper contains 77 references and 17 tables.

Thermal Properties of Porous Foods

by K. Wallapapan, V. E. Sweat, K. C. Diehl and C. R. Engler, Agricultural Engineering Department, Texas A&M University, College Station, TX 77843.

A comprehensive and extensive literature review of thermal properties of porous foods is presented. Experimental and estimation models reported in the literature were conveniently tabulated. Detailed discussions of measurement techniques and some practical estimation techniques were also included. The paper contains 38 references and 7 tables.

Thermal Properties of Frozen Foods

by D. R. Heldman, Food Engineering Department, Michigan State University, East Lansing, MI 48823.

Numerical values of the thermal properties of frozen foods are essential in order to establish the refrigeration requirements for freezing, freezing times and frozen food storage conditions. The efficiency of the freezing process and control of product quality depend on these properties. This paper presents prediction models for thermal properties of frozen foods along with experimental data for comparison with predicted values. The paper contains 34 references, 9 figures and 1 table.

(c) Colligative

Water Activity and Other Colligative Properties

by H. K. Keung, Department of Food Science and Human Nutrition, Washington State University, Pullman, WA 99164-6330.

The concept of water activity has received much attention from food scientists and engineers in recent years. In this paper, the thermodynamic basis of water activity and other colligative properties of foods is discussed. The significance of water sorption properties in foods is reviewed. Techniques for determination and prediction of water activity and sorption isotherms in foods are summarised. Water sorption data for selected food products are presented. The paper contains 180 references, 15 figures and 9 tables.

(d) Quality

Quality Changes in Frozen Foods

by R. P. Singh, Agricultural Engineering Department, University of California, Davis, CA, and D. R. Heldman, Department of Food Science and Human Nutrition, Michigan State University, East Lansing, MI 48824.

Property data useful in describing quality changes in foods during frozen storage is presented. Application of these data in computer-aided simulation of shelf life is discussed. The paper contains 28 references, 5 figures and 5 tables.

Microbial Population, Enzyme and Protein Changes During Processing
by D. R. Thompson and J. Norwig, Agricultural Engineering Department, University of Minnesota, St Paul, Minnesota, USA.

Many changes occur in foods during processing, and there are many ways of representing those changes. This report tabulates previously-published kinetic data on changes in microbial populations, enzyme activity and protein reactivity during processing and storage of food. The paper contains 256 references and 5 tables.

Effect of Processing on Kinetics of Nutrient and Organoleptic Changes in Foods

by R. Villota and J. G. Hawkes, University of Illinois.

The main aim of this paper is to summarise recent investigations on the kinetics of quality degradation, with particular regard to thermal processing, in order to provide a clearer picture of what has been accomplished on the kinetics of real food systems and to point out areas for further research. The paper contains 218 references, 5 figures and 9 tables.

Kinetics of Physical Changes in Foods

by D. B. Lund, Department of Food Science, University of Wisconsin-Madison, Madison, WI 53706.

Physical changes in foods as a result of processing often dictate the industrial viability of a process. For engineers to design processes, they need to consider changes in physical properties as a result of the process route. This paper reviews several concepts describing the effect of process variables (particularly time and temperature) on physical properties of foods. The paper contains 40 references and 5 tables.

Kinetics of Flavour Changes in Foods

by L. R. Wilson, Food Technology Department, Iowa State University, Ames, IA.

This paper reviews the various measurements and data-handling techniques used to measure and interpret the kinetics of flavour changes in foods. A compilation of available kinetic data is presented to aid the successful design and operation of food processing systems. The paper contains 84 references and 11 tables.

The work represented by these papers forms a starting point from which continued updating and enhancement of the data should proceed. Each of the topic areas in this volume will be updated when new data are available. New topics will also be added in an effort to encompass a large cross-section of the food properties area. Comments or suggestions regarding the papers included in this volume or which should be included in the next are welcomed.

REFERENCE

Okas, M. R. (Ed.) (1987). *Physical and Chemical Properties of Food*, ASAE Publication No. QO986, St Joseph, MI, U.S.A.

DISCUSSION

J. de Baerdemaeker: Since the data sources are likely to be the same, do you envisage differences in the use of these data, as in the computer models such as COSTHERM? *M. R. Okos* felt that there would be, such as in the example cited. Exchange of programs was being considered. *W. E. L. Spiess* emphasised the industrial and commercial objectives of the COST 90bis work and asked how far US industry was involved in the NC136 Project. *Okos* said that the Project was partly academic, partly for industry. For example, new aseptically-processed foods are being measured for industry; an AIChE consortium is providing input and some grants have been made by industry. *Spiess* asked what projects other than data collection are included in Project NC136. *Okos* replied that aseptic processing, drying and the processes involved in generating physical data were included. An important objective was the avoidance of inter-State duplication in the USA.

PPDS: the UK Physical Properties Data Service for the Chemical and Process Industries

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SUMMARY

The application of validated thermophysical property data in the design and operation of plant in the major process sectors is discussed. Particular emphasis is given to computerised databases, with 'user-friendly' driver programs to access data values and also capable of being interfaced to a wide range of applications programs. General requirements are given for the development of robust thermophysical property software packages and associated databases. PPDS, the Physical Property Data Service, which is used worldwide in the chemical engineering industry, is then described in detail.

1. INTRODUCTION

1.1 Process Plant Design

The design and operation of almost all plant in the process sectors of industry requires reliable physical property data. The type of properties and the conditions at which the data are required can vary markedly from sector to sector. The petroleum industry, for example, often deals with fairly specific groups of chemicals and many data correlations and estimation procedures have been developed, notably the work of the American Petroleum Institute (API). In power generation the main requirement is for accurate property values for water and steam; for some new technologies, e.g. synthetic fuels, property values are often required over wide ranges of temperature and pressure; in other industries, such as pharmaceuticals and agrochemicals, the number of compounds in

everyday use is very large. Table 1 gives a list of some major industrial sectors where validated physical property data are essential.

The main problem facing the design engineer is that even if they are available at the required process conditions the data may be difficult to find and to assess. When designing plant and equipment, no useful calculations, estimations or designs can be made without physical property data of some kind. Furthermore, the data used must be appropriate to the conditions; simple ideal-state calculations are usually insufficient to describe a process adequately.

Extensive data for all thermophysical properties is generally available only for a limited set of pure components, whereas in most instances the user requires data for multicomponent mixtures over a wide range of temperatures and pressures.

The growth of interest in reliable data packages has been markedly influenced by both economic and environmental factors. Some 10–15 years ago, when both energy and materials were apparently in plentiful supply, the reliability and accuracy of property data used in plant design was not considered to be of primary importance. This is no longer the case. In many applications it is now apparent that high-quality data must be used in the design to ensure that the plant is efficient in operation and can be manufactured at a competitive price. Reductions in manpower in design departments and the greater need to respond quickly and competitively to tenders have also contributed to the increased interest in data packages.

There now exist a number of computerised design packages for the process industry, which range from the design of heat exchangers to sophisticated systems for process simulation and flowsheeting. Many of these packages require large numbers of property values and the input of data by hand for these systems is no longer desirable, or in some cases even feasible. Recognising this fact both the developers and users of design software have begun to appreciate the usefulness of computerised physical property packages and data bases which can provide reliable data for the

TABLE 1
MAJOR PROCESS PLANT SECTORS

Petrochemical	Synthetic fuels
Chemical	Metals and minerals
Petroleum refining	Pulp and paper
Pharmaceutical	Food
Oil and gas	Agrochemicals
Power generation	Biotechnology

specified properties of fluids and fluid mixtures, and which can be easily and robustly linked to a wide range of applications programs.

Only the major industrial companies can afford the time and manpower to set up and maintain in-house property databases to suit all potential applications. A more realistic solution is to subscribe to a commercial system, which may involve the purchase of a full software licence or occasional use on a computer bureau on a pro rata basis.

1.2 Physical Property Databases

Three types of system for data retrieval, not necessarily computerbased, may be considered:

- (a) Bibliographic—lists of abstracts of original publications are available from many library and information sources. These systems are usually keyword driven and may produce only brief references, but some systems reproduce original experimental data.
- (b) Raw data—which may appear in reference books or handbooks, or be stored on computer files. The data may be in their original form, with several sets of data in different units, or they may have been processed to give tabulated values for ease of interpolation and extrapolation.
- (c) Computerised databases—this is a natural development from the two cases above. The experimental data for a particular property of a substance are collected and carefully evaluated, and fitted to a suitable correlating equation. Software can then be produced to derive values at any specific conditions. One major advantage in the process design area is that this system can be interfaced to applications programs which require physical property data.

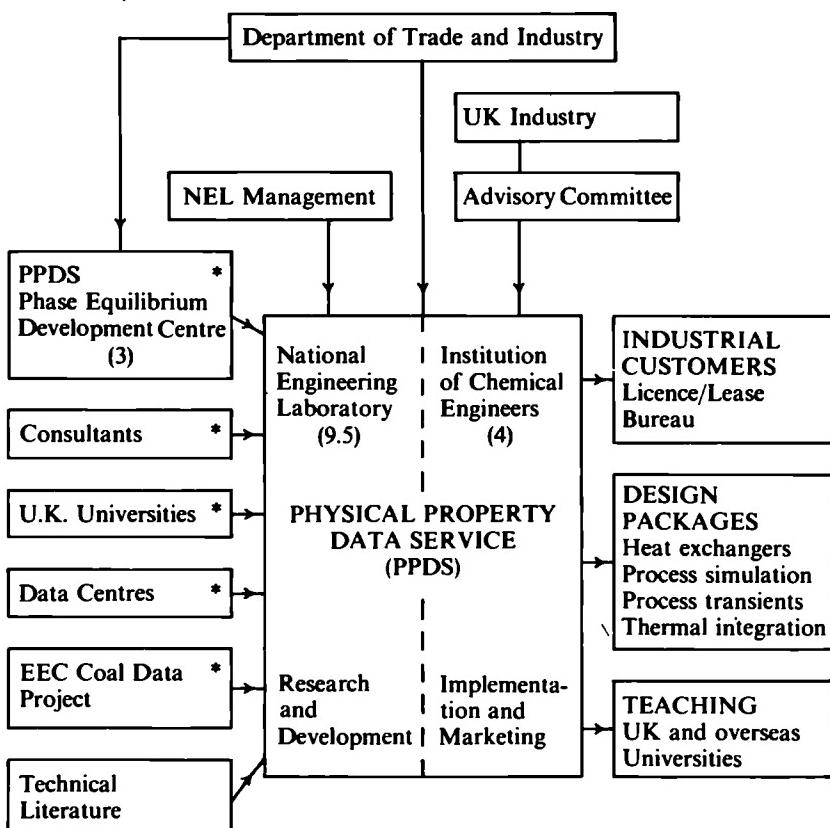
Hilsenrath¹ produced a summary of on-line interactive databanks, and at the previous COST 90 Seminar, Eckermann² gave a description of the DECHEMA data system, with emphasis on the bibliographical section. Other thermophysical property databases for pure components have been developed as part of the DIPPR project in the USA^{3,4} and in Japan.⁵

1.3 PPDS

The Physical Property Data Service (PPDS) package was originally based on software and databanks provided by two leading British firms, and was developed as a commercial package by the Institution of Chemical Engineers (IChemE) with support from the UK Department of Trade and Industry. The National Engineering Laboratory (NEL), one of the UK

government's research and development laboratories, has carried out fundamental work on physical properties for over 25 years and has gained an international reputation in many areas. NEL had developed extensive property databases and estimation packages, and had provided services in the physical property areas to industrial users and data organisations. In 1982 NEL took over formal responsibility for PPDS, and now develops and markets the system in conjunction with IChemE.

In addition to the general maintenance and development of PPDS, there is an underlying experimental research programme at NEL and close



() Staff effort in man-years p.a.

* Data activities wholly or partially funded by PPDS

Fig. 1. Organisation of PPDS and its relation to data users.

collaboration with universities, industry and data centres. PPDS is available to users through licence or bureau use, and is interfaced to a number of major design programs. In addition it is available at several UK universities as a teaching aid in process engineering. This is summarised in Fig. 1.

The following section discusses the requirements for a thermophysical properties software and database package, using the experience gained in the production of PPDS and the development of techniques for data analysis, and the remaining sections give a brief review of the PPDS system.

2. PROGRAM AND DATABASE DESIGN

2.1 Software Packages

The development of a thermophysical properties package for maximum benefit in the chemical and process industries should have the following aims:

- (a) To provide reliable, traceable and, wherever possible, assessed values of the thermophysical properties of fluids and fluid mixtures over a wide range of conditions to an accuracy commensurate with industrial needs.
- (b) Be capable of access and use by non-specialists.
- (c) Allow direct access by a flexible conversational package.
- (d) Have the facility to be interfaced with other packages.

The production of any major software package should combine the requirements of the anticipated users with the need to minimise overheads in the development and maintenance of the system. The normal practices of good software engineering should be implemented to produce a flexible, modular package, with particular consideration given to the following areas:

- (a) Maintainability—there should be a logical relationship between different sections of the program, so that it is easy to alter the coding or find errors.
- (b) Reliability—the package should provide input data checking where possible, and should always attempt to return an answer (at default conditions if necessary). This latter feature is particularly important if the program is linked to an application program.
- (c) Efficiency—both in code design and run-time operation. A suite of test examples to check all aspects of the system should be developed.

- (d) Comprehensiveness—the most up-to-date methods and algorithms should be implemented and a wide range of input/output options should be provided.
- (e) Ease of use—a well-designed interactive interface with on-line help facilities, combined with good documentation, should cater for both new and regular users.

2.2 Database Development

The design of a physical properties database requires decisions to be made on the choice of the compounds or materials and the relevant properties, the way the data are to be stored and the general organisation of this information. These questions are closely related to end-user requirements and restrictions (computer type, storage limitations, file structure), the accuracy and reliability of the retrieved data, the algorithms for accessing and processing the data, and the procedures for quality control and file management. For the particular case of a physical properties database several alternative methods may be considered:

- (a) raw data arising from direct experimental measurement;
- (b) normalised data (raw data converted to a standard set of units and reference states);
- (c) correlated or smoothed data (selected and assessed data represented as a function of one or more independent variables);
- (d) structural or molecular correlation parameters (experimental data represented by parameters characteristic of molecular structure or physical constants).

Although ideally it would be desirable to have several types of data stored in the one system, severe limitations arise in practice if this is attempted. The data files become large and expensive to maintain. Practical difficulties arise from the storage of multiple data sets of different accuracy and reliability for the same property, from the need for algorithms for interpolation and extrapolation, and the use of such data in mixture calculations.

Selected and smoothed or correlated data are preferable for most applications, including physical property evaluation, for their compactness and speed. The correlation approach is suited to applications requiring direct access at the software level from another program. The use of molecular and structural parameters is potentially an elegant means of storing thermophysical properties, but the techniques are not yet sufficiently well developed for most properties.

The best approach for physical property databases would appear to be to store data records for pure components as a set of physical constants plus the coefficients of correlating equations. The type of representative equation requires a great deal of study. Many properties are correlated using simple equations, often polynomials, without too much thought to the functional form. This is acceptable if the user remains aware of the limitations of such representations, usually with regard to extrapolation of the data, but this is not always the case, particularly if the equation form is hidden in badly-annotated software. The form of representative equation for physical property correlations should be influenced by the following considerations:

- (a) the functional form of dependence suggested by theory;
- (b) the known physical behaviour of a property for a wide range of compounds;
- (c) the provision of a reliable and accurate representation over a wide temperature (and/or pressure) range;
- (d) the maintenance of internal thermodynamic consistency;
- (e) the minimisation of the number of terms in the equation with all coefficients having full statistical significance;
- (f) the usefulness of the end-product with regard to the complexity and speed of evaluation.

3. THE PPDS PROGRAM

3.1 Introduction

The PPDS software package is a coherent and mutually compatible suite of computer codes and databanks, which provides most of the thermo-physical property information, including phase-equilibria calculations, for pure fluids and fluid mixtures over a wide range of conditions. The system has been structured to be both cost and time effective and portable. Data may be accessed using a conversational 'front-end' program, or the package may be directly linked to applications programs. PPDS is essentially a data evaluation, rather than a bibliographical system, but references to the original data sources can be provided on request. The overall structure of the system is shown in Fig. 2.

Most process engineering calculations are concerned with two kinds of situation:

- (a) Phase equilibria—given the overall stream composition, what is the phase at the required operating conditions, and, if it is a multiphase system, what are the compositions of each phase?

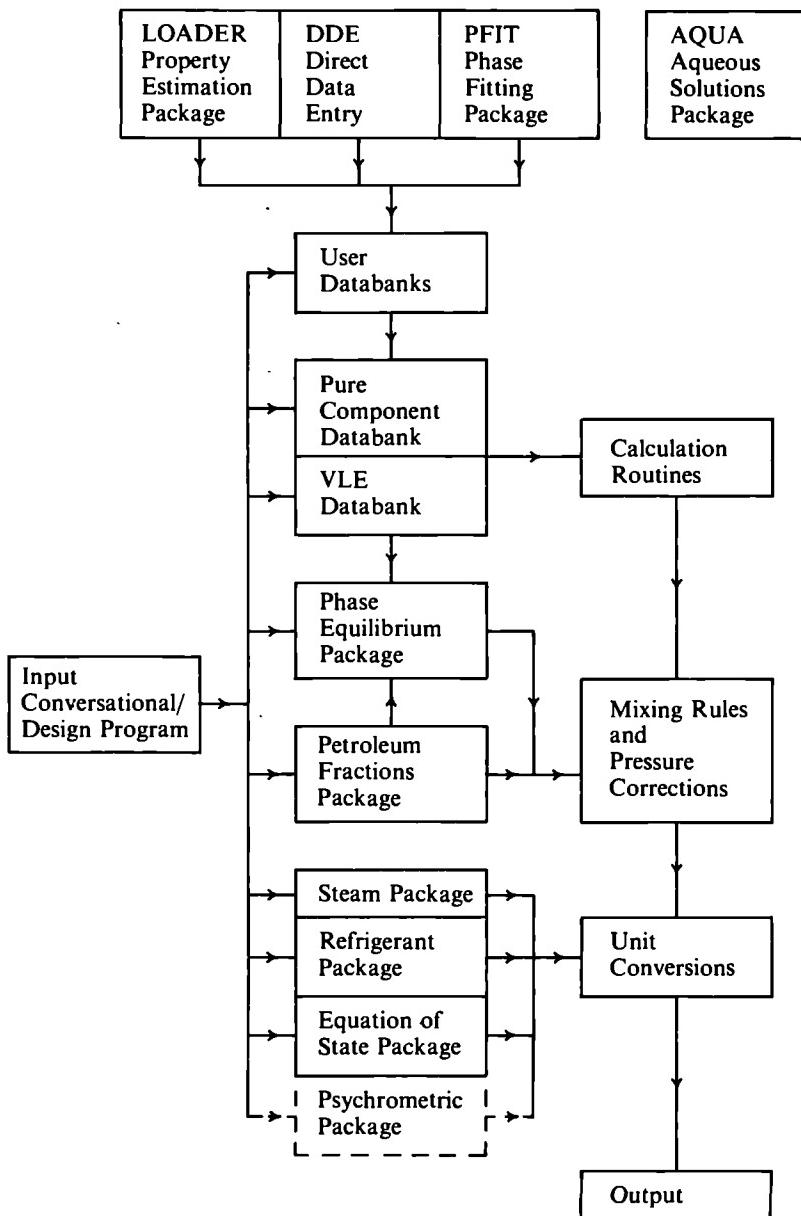


Fig. 2. The Physical Properties Data System.

- (b) Physical properties—given the conditions (temperature, pressure and compositions), what are the ‘best’ values of the required physical properties?

3.2 Phase Equilibria

The PPDS phase equilibrium package can perform a range of calculations using a variety of different methods as detailed in Table 2.

The associated vapour–liquid equilibrium (VLE) databank contains binary interaction information for about 700 pairs of components and is being constantly updated, but is limited by the amount of experimental data available. If the user has interaction data from another source, he may include these at the appropriate point in the program dialogue. If the experimental phase-equilibrium data are available, the ancillary program PFIT may be used to regress the data to obtain the interaction information for any chosen method (except UNIFAC).

An example of an isothermal flash calculation for a three-component mixture is shown in Fig. 3.

3.3 Physical Properties

The pure component databank currently contains 860 compounds (804 organic, 56 inorganic). One record is used for each compound and contains

TABLE 2
(a) TYPES OF CALCULATION

Vapour-liquid flash	Constant vapour fraction
Liquid-liquid flash	Isochoric flash
Bubble point	Isenthalpic flash
Dew point	Isentropic flash
Boiling range	

(b) METHODS AND MODELS

Method	Type of model
Redlich–Kwong–Soave	Cubic equation of state
RKS (API modification)	Cubic equation of state
Peng–Robinson	Cubic equation of state
Lee–Kesler–Plocker	Corresponding states
Wilson A	Activity coefficient
UNIQUAC	Activity coefficient
UNIFAC	Activity coefficient using a group contribution method

PHYSICAL PROPERTY DATA SERVICE

PPDS PROGRAM VERSION: 10.08

PROGRAM START AT: 15:31:07 11-JUL-86

TITLE?

"TEST EXAMPLE"

NO. COMPS?

3

QUANTITY CODE?

MOLE-FRAC

CODE NOS AND QUANTITIES?

63, 0-3, 93, 0-3, 146, 0-4

VLE METHOD?

TYPE THE VLE METHOD: 0=NO VLE, 1=RKS, 2=WILSON A,
3=UNIFAC, 4=PENG-ROBINSON,
5=RKS(API), 6=LKP,
7=UNIQUAC, 8=UNIFAC(LLE).

2

WHICH VLE CALC?

1

DEFAULT CODE?

1

NO. CONST. and VAR. PROPS?

18,20

TEMP. UNITS?

C

PRESS. UNITS?

ATM

NO. DATA POINTS?

1

(T,P) VALUES?

75, 1

OUTPUT UNITS CODE?

SI

CHANGE, CHECK, GO, STOP?

GO

STREAM DEFINITION:

CODE	FORMULA	BANK NAME	GIVEN NAME
63	H2O	WATER	63
93	C2H6O	ETHANOL	93
146	CH4O	METHANOL	146

COMPOSITION: TEST EXAMPLE

COMPONENT	WT.	WT.PERCENT	MOL	MOL.PERC
63 WATER	5.406	16.871	0.300	30.000
93 ETHANOL	13.821	43.132	0.300	30.000
146 METHANOL	12.816	39.997	0.400	40.000

MIXTURE: 32.043

1.000

PPDS VLE PACKAGE: V7-07

METHOD: WILSON A

OPTION: FLASH CONST P,T

DEFAULT: IDEAL

GIVEN TEMPERATURE: 348.150 DEG K
GIVEN PRESSURE: 101325.000 N/M2

PHASE MOLE FRACTIONS	LIQUID(X)	VAPOUR(Y)
63 WATER	0.3920929	0.2138215
93 ETHANOL	0.2934197	0.3061578
146 METHANOL	0.3144875	0.4800208

TOTAL MOLAR FLOW	0.483	0.517
TOTAL MASS FLOW	14.821	17.222

Fig. 3. Specimen input and output for a VLE calculation.

basic constants (molecular weight, critical properties, safety information, thermochemical data, etc.) plus the coefficients of the correlating equations for ideal gas and saturated liquid properties. For historical reasons, many different types of correlation equation are used, but future versions of the databank will include only the coefficients for the recommended equation for each stored property.

If a user wishes to modify the constants or correlate a set of new experimental data the application program DDE (Direct Data Entry) is available for this purpose. The changes may be run-temporary, or the new data records may be written to a private database for future use.

The stream constants and variable properties given in Table 3 are available as output.

The temperature range is from the melting point to just below the critical point for liquid properties and from the melting point to 1000 K for vapour properties. Pressure corrections in the vapour phase are made using the generalised corresponding states approach of Lee and Kesler⁶ for the thermodynamic properties and well-established techniques^{7,8} for the

TABLE 3
(a) PHYSICAL CONSTANTS

Formula weight	Flash point
Critical temperature	Lower flammability limit
Critical pressure	Upper flammability limit
Critical volume	Autoignition temperature
Melting point	Solubility parameter
Boiling point	Acentric factor
Parachor	Reference vapour entropy
Vapour heat of formation	Acentric factor of homomorph
Liquid heat of formation	Dipole moment

(b) VARIABLE PROPERTIES

Vapour heat capacity	Liquid heat capacity
Vapour viscosity	Liquid density
Vapour thermal conductivity	Liquid thermal conductivity
Vapour enthalpy	Liquid enthalpy
Vapour density	Liquid density
Vapour entropy	Liquid entropy
Vapour Gibbs free energy	Liquid Gibbs free energy
Vapour pressure	Surface tension
Enthalpy of vaporisation	Entropy of vaporisation
Liquid coefficient of cubical expansion	Total heat of formation

PHASE MOLE FRACTIONS	LIQUID(X).	VAPOUR(Y).
63 WATER	0.3920929	0.2138215
93 ETHANOL	0.2934197	0.3061578
146 METHANOL	0.3144875	0.4800208
TOTAL MOLAR FLOW	0.483	0.517
TOTAL MASS FLOW	14.821	17.222

PROPERTY VALUES HAVE TAKEN ACCOUNT OF THE ABOVE PHASE FRACTIONS

STREAM CONSTANTS: TEST EXAMPLE

COMPONENT	63	93	146
1 MOLECULAR WEIGHT	18.020	46.069	32.040
2 CRITICAL TEMPERATURE	DEG K	647.300	513.920
3 CRITICAL PRESSURE	N/SQ.M	0.2212E+08	0.6137E+07
4 CRITICAL VOLUME	M3/KGMOLE	0.05631	0.1669
5 MELTING POINT	DEG K	273.150	159.000
6 BOILING POINT	DEG K	373.150	351.440
7 PARACHOR	ST-4/KMOLE	52.118	128.278
8 VAP. HT. OF FORMATN.	MJ/KGMOLE	-241.828	-234.814
9 LIQ. HT. OF FORMATN.	MJ/KGMOLE	-285.835	-275.967
10 FLASH POINT	DEG K	0.000	285.000
11 LOWER FLAMM. LIMIT	PERCENT	-1000.00*	3.300
12 UPPER FLAMM. LIMIT	PERCENT	-1000.00*	19.000
13 AUTOIGNITION TEMP.	DEG K	-1000.00*	698.000
14 SOLUBILITY PARAMETER	RT(CAL/CC)	23.400	12.730
15 ACENTRIC FACTOR		0.3440	0.6440
16 VAPOUR ENTROPY	KJ/KGMOLE K	188.800	281.400
17 A.F. OF HOMOMORPH		0.01100	0.1530
18 DIPOLE MOMENT	DEBYES	1.820	1.730

STREAM VARIABLES. TEST EXAMPLE

		LIST 1
TEMPERATURE	DEG K	348.150
PRESSURE	N/SQ.M	101325
MOLECULAR WEIGHT	LIQUID	30.659
MOLECULAR WEIGHT	VAPOUR	33.337
1 VAP. HEAT CAPACITY	KJ/KG K	1.625
IDEAL GAS VALUE.	KJ/KG K	1.572
ADJUSTED RATIO CP/CV		1.207
IDEAL RATIO CP/CV		1.189
2 VAPOUR VISCOSITY	CENTIPOISE	0.01116
IDEAL GAS VALUE.	CENTIPOISE	0.01116
3 VAPOUR CONDUCTIVITY	W/M K	0.02067
IDEAL GAS VALUE.	W/M K	0.02067
4 VAPOUR ENTHALPY	MJ/KGMOLE	2.295
IDEAL GAS VALUE.	MJ/KGMOLE	2.519
5 LIQUID HEAT CAPACITY	KJ/KG K	3.238
6 LIQUID CONDUCTIVITY	W/M K	0.2228
7 LIQUID DENSITY	KG/CU.M	782.350
8 LIQ.CU.EXPAN. COEFF.	I/K	0.1431E-02
9 LIQUID ENTHALPY	MJ/KGMOLE	-36.488
10 LIQUID LATENT HEAT	MJ/KGMOLE	38.699
11 LIQ. SURFACE TENSION	N/M	0.03588
12 LIQ. VAPOUR PRESSURE	N/SQ.M	88621.1
13 LIQUID VISCOSITY	CENTIPOISE	0.3705
14 VAPOUR DENSITY	KG/CU.M	1.192
IDEAL GAS VALUE.	KG/CU.M	1.167
COMPRESSIBILITY		0.9792
15 TOT. HEAT OF FORMATN.	MJ/KGMOLE	-239.792
16 VAPOUR ENTROPY	KJ/KGMOLE K	-48.096
IDEAL GAS VALUE.	KJ/KGMOLE K	-47.624
17 LIQUID ENTROPY	KJ/KGMOLE K	-101.674
18 ENTROPY OF EVAPORTN.	KJ/KGMOLE K	111.068
19 VAPOUR FREE ENERGY	MJ/KGMOLE	19.040
IDEAL GAS VALUE.	MJ/KGMOLE	19.099
20 LIQUID FREE ENERGY	MJ/KGMOLE	-1.091

Fig. 4. Example of output for stream properties calculation.

transport properties. No pressure corrections are currently applied in liquid phase. Mixture properties for systems of up to 20 components are calculated from the pure component values using proven mixing rules.

A wide range of units is available at both the input and output stages, but internally SI units are used throughout. Warning messages are provided when the input conditions are out of range, although appropriate default values are returned so that design programs linked to PPDS will not fail.

A package is provided to allow petroleum fractions to be used as pseudo-components. The fractions are characterised by molar average boiling point, volume average boiling point, API gravity and molecular weight (if known).

In conversational mode a flexible free-format input is available with keyword or numeric data entry, various levels of on-line help, type-ahead facility and full check and re-run capabilities. Log files of each run are maintained for future inspection.

An example of a property calculation is shown in Fig. 4, where the stream is the same as that used in the earlier phase-equilibrium calculation (Fig. 3).

4. SPECIAL PACKAGES

4.1 Water Substance

Water is the most commonly used process fluid and has applications ranging from power generation to geothermal technology. In many instances property values must be certified to be of appropriate accuracy for the particular application. The International Association for the Properties of Steam (IAPS) is the organisation currently responsible for the formulation and standardisation of the properties of water substance, and NEL has taken an active part in the work of this body.

PPDS supplies four separate packages to suit a number of applications and computer environments.

IAPS82 is based on the latest international standards for both thermodynamic and transport properties, and is recommended for use where the highest precision and widest operating range is required. Although optimised for speed, it is mainly suitable for mainframe operation.

IAPSPH is a version of IAPS82 which allows the use of pressure and enthalpy as input variables.

STEAM is the package based on the older 1967 International Formulation Committee recommended equations. Although superseded

by IAPS82, this package retains status for certain contractual purposes and is therefore implemented in the main PPDS package.

FASTWS is a subprogram developed to meet the need for a fast, robust package suitable for the more limited range of thermal engineering calculations, but still giving values in close agreement with the standard packages. Based on Gibbs function formulations for water and steam, it gives large increases in speed of operation, which makes it suitable for microcomputer use.

4.2 Psychrometric Package

Although psychrometric charts are still a valuable tool for solving problems involving moist air, the need for a computer package to link to the increasing range of design packages is evident. PSYCHO is a fast, robust subroutine package for the psychrometric, thermodynamic and transport properties of moist air over a temperature range from -100 to 200°C and at pressures up to 5 MPa.

The input variables are absolute pressure, dry bulb temperature and one of the following humidity indices:

- wet bulb temperature,
- dew point temperature,
- % relative humidity, or
- humidity ratio.

4.3 Refrigerants Package

Reliable physical property values for refrigerants are required in many areas, and this subroutine package is based on a wide-ranging equation of state for evaluation of the thermodynamic properties and up-to-date

TABLE 4

<i>Freon</i>	<i>Formula</i>	<i>Name</i>
R11	CCl_3F	Trichlorofluoromethane
R12	CCl_2F_2	Dichlorodifluoromethane
R13	CClF_3	Chlorotrifluoromethane
R13B1	CBrF_3	Bromotrifluoromethane
R14	CF_4	Tetrafluoromethane
R22	CHClF_2	Chlorodifluoromethane
R113	$\text{C}_2\text{Cl}_3\text{F}_3$	Trichlorotrifluoroethane
R114	$\text{C}_2\text{Cl}_2\text{F}_4$	Dichlorotetrafluoroethane
R717	NH_3	Ammonia
R502	—	Azeotrope of R22 and R115

TABLE 5

Ammonia	Sodium cyanide
Calcium chloride	Sodium hydrosulphite
Ethylene glycol	Sodium hydroxide
Hydrochloric acid	Sodium hypochlorite
Oleum	Sodium sulphide
Potassium chloride	Sulphuric acid
Potassium hydroxide	Nitric acid
Sodium carbonate	Phosphoric acid
Sodium chloride	

correlations produced by NEL for the transport properties. The regions covered are saturated liquid, saturated vapour and the superheated vapour, and the compounds given in Table 4 are included.

4.4 Aqueous Solutions Package

AQUA is a stand-alone package for the liquid-phase thermodynamic and transport properties of a number of acid and salt solutions (Table 5).

4.5 Equation of State Package

The Imperial College Thermophysical Properties Data Centre has produced high accuracy correlations of reliable experimental data for a selected set of industrially-important fluids. This package is available separately or as an option to PPDS and currently includes the following compounds:

Ethane	Propane
Ethylene	Propylene
Hydrogen	Carbon dioxide
Oxygen	Argon
Methane	Helium-4
Nitrogen	Heavy water

5. PHYSICAL PROPERTY ESTIMATION—THE LOADER PACKAGE

The PPDS main databank provides information on 860 industrially-important chemicals, but thousands more are in general use, particularly in the pharmaceutical, fine chemical and agrochemical sectors. The design

engineer is faced with the task of obtaining data for particular compounds of interest. Usually only limited data are available and additional data have to be estimated. In the majority of cases, the process stream under consideration will probably be a complex mixture with the properties for other components available from a system such as PPDS.

The LOADER package provides an elegant solution to these problems. It is designed as a sophisticated property estimation program, but, more importantly, the final output is a complete data record identical with that used in PPDS for inclusion in a private data bank. Subsequently records in this bank may be accessed from the PPDS package, as shown schematically in Fig. 5.

The wide variety of property estimation procedures range from those based on sound theoretical principles to those which are highly empirical.⁹ Most methods have been developed for limited sets of compounds (e.g. alkanes or hydrocarbons), and are not easily applied to other systems. Extensive evaluation of the available methods by NEL staff has resulted in the production of a suite of estimation methods with a hierarchical structure,¹⁰ and this module is central to the operation of LOADER.

The package may be operated at a number of levels, depending on the amount of data available, but in each case a full range of property estimation and correlation is carried out and a complete data record is

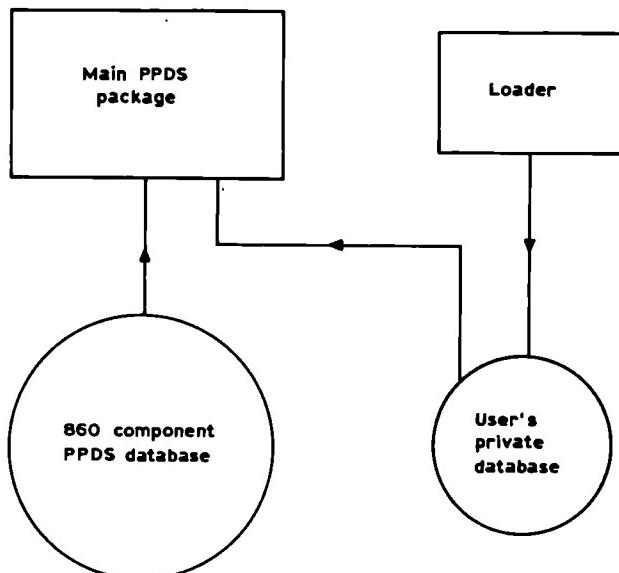


Fig. 5. Interaction between LOADER and PPDS.

produced. The minimum input data set consists of the molecular weight, the normal boiling point and the chemical structure. In this case the properties are entirely estimated.

If some experimental data are available for a particular property (perhaps over a limited temperature range), then the program will blend these with estimated data to produce a more reliable set of data to cover the complete temperature range. If a wide range of experimental data is available then these can be fitted directly to the appropriate correlating equation.

The program is run in conversational mode, similar to the main PPDS program, which provides dual-level dialogue (for novice and experienced users), keyword entry and extensive help facilities. This flexibility is particularly useful in the experimental data input section, where multiple data sets can be entered and individual data points can be added, removed or restored with immediate re-run facilities. In all cases thermodynamic consistency is maintained between the calculated properties.

6. ACCESS TO PPDS

The PPDS package is currently written in ANSI FORTRAN IV for maximum portability in a scientific environment. The machine-dependent parts of the coding (e.g. file-handling, unit numbers) have been centralised in one module, and the package has now been successfully implemented on a wide range of mainframe and minicomputers including IBM, DEC, UNIVAC, CDC, VAX and PRIME. Some of the specialised packages mentioned earlier are also suitable for microcomputer use.

The main system can be obtained in source code form as a sublicence or lease, with or without annual updates and maintenance. The system is also available, in some cases in conjunction with major design packages, on the following bureaux:

Control Data Ltd	Worldwide
Geisco Mk III	Worldwide
UCC	UK, USA
SIA	UK, Euronet
Scicon Computer Services	UK
Computer Centrum Groningen	Netherlands
Aquitaine Systems	France
Datacall	UK
TDS, Inc	USA

The PPDS Data Module is a new hardware development in which the full PPDS program and databanks have been implemented in firmware on a portable, microprocessor-based unit. The Data Module can be linked to a VDU or printing terminal using a standard interface and the program may be run in conversational mode. Alternatively it may be linked to a microcomputer on which an applications program is running. The module acts as an intelligent peripheral and can be accessed for data values as and when required.

7. FUTURE DEVELOPMENTS

As with any major software package, the PPDS system is subject to a continuous schedule of development and maintenance. In the case of a thermophysical properties system, this must be influenced to a large extent by the requirements of the users. Foremost amongst the developments now being undertaken are:

- (a) A major rewrite of the package in FORTRAN 77, with emphasis on a simplified modular structure and the production of an alternative screen-orientated input/output facility.
- (b) The constant re-evaluation of the present databank and the inclusion of new compounds.
- (c) The development of improved methods for pressure corrections and mixing rules.
- (d) Evaluation of new prediction methods and their inclusion in the LOADER package as appropriate.
- (e) The development of new specialised packages, e.g. heat transfer fluids, lubricants.
- (f) A new version of the Data Module which includes both PPDS and LOADER.
- (g) The production of subpackages for the microcomputer market, with particular emphasis on specific application areas.

8. CONCLUSION

This volume is primarily concerned with the physical properties of foods, whereas this chapter describes a commercial package for thermophysical properties of non-food fluids for process engineering use. Nevertheless, many of the principles and techniques used in the development of the PPDS package have wide application and should prove beneficial in the production of any similar package for properties of foods.

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DISCUSSION

E. Rotstein asked if several equations of state were available in the package. *A. C. Scott* replied that for the general commercial package of 860 different substances, there was just one generalised equation of state for the pressure-dependent properties calculation in the program, based on the Lee-Kesler corresponding states equation. The different packages available for specific substances use different equations of state. *E. Kress-Rogers* asked about error estimation to which *Scott* replied that it was difficult to provide probable error estimates for each property in the general program but that if that were important to a particular user, arrangements could be made to provide it for him. Otherwise, they try to provide the 'best possible' values in each set of circumstances.

Part 6

GENERAL REVIEW AND OUTLOOK

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COST 90bis: Conclusions and Outlook

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Many viewpoints could be expressed on projects like COST 90bis. The project could be analysed from an international or national point of view, or from an institutional or individual point of view. The scientific results and the value for money could also be considered. It will not be possible here to cover all aspects but rather to voice some thoughts on matters which have come up over the years.

THE ORGANISATION

COST 90bis is a 'federal' system in that its budget covers the expenses for meetings, etc., but the work itself has to be financed by each individual country.

The system of COST has some considerable advantages. Each country remains independent and may choose how to organise its research work and how to finance it. With this system the administration procedures for COST remain simple as little money has to be allocated to individual countries or persons; the system is also quite flexible and adaptation to the programme can be made easily. COST projects are well defined, and limited in time and resources. The size is such that they are 'reviewable' at any time and they are based on 'person-to-person contact'. The system relies on the enthusiasm of those who collaborate, which enhances the quality of the work; the participants are not just 'official delegates'.

These structures, however, create some disadvantages which should not be overlooked. The preparatory steps are time-consuming, but very

important, because each country *must* define the contribution that it will make. If such a contribution is not guaranteed, the individual scientist cannot participate in the experimental work. In general, such preparatory work needs to be performed more carefully within the COST member countries.

Another disadvantage is the small degree of control over the performance of the tasks. The coordinator of a subgroup can never rely upon the execution of the work decided upon at a meeting. The participating institute may have other priorities.

INTERNATIONAL COOPERATION

COST projects promote the sense of a united Europe. It is important for future development in Europe that this way of thinking and working penetrates all levels involved: politicians, administrators, scientists, laboratory personnel and so on.

This type of collaborative project reduces the risk of isolation of scientists, institutes or even countries.

The projects create contacts and promote communication at all levels which is of special importance to scientists and students. It gives the participants the opportunity to meet, and in this way other subjects and projects are also discussed, initiated and sometimes fruitfully completed.

It might also be possible within the framework of these projects to exchange scientists and students between laboratories, thereby gaining even more from this type of cooperation.

THE WORK AND ITS QUALITY

COST projects are both *scientific* and *technological*. These aspects have to be properly balanced, as with COST 90 and COST 90bis both sides have their importance and merits. Whereas the technological aspect involves the production and collection of data which industry can apply to its operations, understanding the origin of such data and their methodology constitute the scientific goal. Therefore, although COST work may be financed partly by commercial or industrial funds in some countries, and administered through the corresponding Directorate-General (DG III) of the EC Commission, the scientific input remains important. In both COST 90 and COST 90bis it was found that many participants were willing

to contribute work well beyond their obligations if a particularly interesting problem arose. Finally, the scientific aspect helps to safeguard the quality of the projects.

But technological results must be achieved, otherwise the industrial requirements are not. In this respect COST 90bis should prove to have been more productive than COST 90, even though the data collection system is still far from being optimal.

Therefore, a more appropriate organisation than the present one might be to nominate several centres or individuals (not one centre or one individual) to undertake the data collection which is then no longer merely a scientific achievement, but which is *vital* to technological progress. Other centres, laboratories and individuals may carry out scientific research collaboratively at the applied level (as hitherto) or may wish to study some fundamental aspect. It is only in this way that experts in their fields can be attracted to collaborate if financial inducements cannot be provided.

So far data have been collected which are equally of use for engineering and processing as for quality evaluation (e.g. colour). Data collection probably has to be extended further towards quality evaluation.

It might be advantageous to carry out work on physical properties related to a particular process, but not *too* particular, such as: diffusion and drying, diffusion and blanching. Such work is usually funded more easily.

THE RESULTS

So far the project has mainly resulted in voluntary standardisation of equipment, methods and laboratory practice. It is the intention and hope that these results, through the national representatives, can be spread to other laboratories and industries. It is each country's responsibility to spread the information. If this work is not taken seriously, the results will remain shelved somewhere and the COST project will not fulfil its purpose. A good flow of information must therefore be established in each country. The results of the first COST 90 project are only now being disseminated in some countries, and we cannot expect to see the effects of COST 90bis yet. However, it is expected that all COST 90/90bis results will find profitable use in the future.

The next stage in the work is to *produce* data by means of the methods agreed upon. The subgroups have already produced some such material. As the methods become widely accepted and used, such data will be produced everywhere. It is important to find a good way to collect these results and

make them easily available. This calls for continuing international cooperation.

Unfortunately, industrial interest in the project has not been very extensive. Two reasons can be suggested. As mentioned above, it takes time before this type of work and the results penetrate the industry. The second reason could be that those responsible for the project have not been active enough in 'selling' the project locally. There are different ways of doing this, such as

- seminars and lectures;
- publications;
- courses, etc.

We should try to improve this aspect of our work. Early this year the Commission distributed information about projects involving industries and the countries involved. The project would benefit greatly from more participation by industrial members in the subgroups. *Communication* from and to industry is vital and has to be improved.

THE FUTURE

In the future, two parallel lines of organisation might exist: the larger part should remain as now, i.e. the participants of each country contribute their work according to their ability and their areas of interest. This will maintain a high *scientific standard* and low *administration costs*. For special tasks, financial resources might have to be allocated to some centres. This could be the case for data collection where three or four centres would take on the task of doing the actual work of collecting and processing data in addition to contributing data from their own programmes. The creation of an entirely 'new' centre for this purpose could be expensive and too inflexible.

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What Next in European Cooperation on Physical Properties of Foods?

RONALD JOWITT
COST 90bis Project Leader

SUMMARY

This chapter reproduces the principal features of the draft proposals adopted by the COST 90bis CCCC in September 1985 as the basis for future collaborative work in Europe on physical properties of foods to follow COST 90bis.

1. INTRODUCTION

Although it is generally agreed that much of value was achieved by COST 90 and will be by COST 90bis, it is also generally agreed that much more remains to be done in relation to ppfs. The first two Projects not only have significant achievements to their credit, they have made it possible for the remaining objectives to be seen and defined much more clearly. It is the purpose of these proposals to identify those newly-defined objectives and the activities needed to pursue them so that decisions may be taken regarding their implementation without delay following the completion of COST 90bis in order that continuity in the Participating States is not lost.

It appears probable that, if the proposed Umbrella programme goes ahead, then the activity proposed herein would be undertaken 'under' that 'umbrella'. There is no reason, however, why any uncertainties which might exist at present regarding the implementation or exact character of the Umbrella programme should hinder or delay consideration of future needs for European cooperation on ppfs.

In this respect, it is regarded as essential that non-Community COST Member States who have contributed so substantially to COST 90 and COST 90bis shall also contribute to these new programmes on ppfs.

2. BACKGROUND

Over the 9 years or so of their joint lives, COST 90 and 90bis will have, through seven subject groups, studied in detail selected aspects of the following physical properties of food topics:

- liquid properties of foods;
- thermal properties of foods;
- sorption properties of foods;
- mechanical properties of foods;
- diffusion properties of foods;
- electrical/optical properties of foods;
- data collection.

All have made significant contributions to their subjects albeit of different kinds as a result of different common interests among the participants in each group. All have benefited from the unique advantages of collaboration within a relatively large group of institutions in different parts of Europe from which the whole is greater than the sum of its parts, as may be seen from what follows.

The original objective was to share among like-minded institutions in Europe a task too large for any one institution or State but which all participants agreed needed to be undertaken and to which they agreed to contribute according to their interests and expertise. This has happened—if not to the stage of completion anticipated, nevertheless to a considerable extent—but other advantages and benefits, not foreseen and possibly of greater value and importance, have accrued.

The first of these is the genuine sharing of knowledge, experience and expertise which has raised the individual and general level of competence of participating institutions. Such an educative benefit was not foreseen. No participant was so advanced or so inexperienced that they did not benefit from this experience.

The second has been the opportunity to become familiar, first on a personal and then on an institutional level, with other similar and allied interests throughout Europe. The importance of this and of its consequent increase in the general awareness of what was going on in these subjects in Europe cannot be overestimated and makes the loss to those who could have participated but did not that much greater.

The third is a rather unique technical benefit central to the subject of ppfs. It has not previously been possible to distinguish between *real*

differences in the values reported by different workers for a particular property of a particular food, and differences arising from different conditions of measurement. Most foods are complex, sensitive substances whose properties vary not only between different, ostensibly identical, examples of the same food, but also in indeterminate ways to often-unrecorded differences in experimental and contextual conditions. An important part of the work of COST 90/90bis has been the 'calibration' of the participants in each exercise by the distribution from a common source of reference food or 'model' materials with known—or believed—uniformity and constancy in respect of the property considered and the adoption, where necessary, of standardised measuring methods. The importance of this 'calibration' of participants is discussed in Chapter 1. Bearing in mind the very great differences between previously-published values for many ppfs, the degree of coincidence which has been achieved as a result of these 'calibration' exercises is remarkable and provides a basis for generating ppfs data largely free from the major uncertainties surrounding previous data, whether they were in apparent conflict with other results or stood alone. It is believed that this achievement is both unique and important: and it would not have been possible except through COST-type cooperation. It has great potential for generating substantial quantities of reliable ppfs data with maximum efficiency.

A fourth related outcome is the confirmation of the importance of contextual information in relation to quantitative ppfs data. The real practical value of ppfs information is expressed by the question: 'How far are *your* data, measured in the context of *your* circumstances, applicable to *my* problem in *my* circumstances?' General ignorance of contextual conditions and of how changes in them affect ppfs values has led some eminent practitioners to the view that other people's ppfs data are of no value to them—or to anyone else—and that there is no acceptable alternative to making measurements on every occasion. Others, faced with the high probability of differences between any measured values they might determine and the values relevant to the context of their technical problem, have concluded that actual measurements are not worth the risk and effort, and that *any* published values are just as likely to be valid for them!

As knowledge of the influence of contextual factors on numerical values for ppfs is extended, the difficulties faced at both these extremes—and intermediately—will diminish and it will become increasingly possible to *adapt* published values—given their context—to the new user's circumstances. It will also become possible to make experimental measurements relate more reliably to the problem to be solved. COST 90/90bis have

highlighted the *importance* of context to ppfs: what is now needed is to *contextualise* ppfs.

3. NEW COOPERATIVE PPFS ACTIVITIES

Against the above background the following can be specified as necessary subjects for further cooperative effort in this field:

- (1) Collection and dissemination of ppfs data, including those arising from ongoing measurements by 'calibrated' participants.
- (2) 'Contextualisation' of ppfs data.
- (3) Applications of ppfs data in food technology and engineering.
- (4) Correlation of physical property measurements with sensory and quality attributes of foods.

1. New Data

A start has been made through the Data Subgroup of COST 90bis on the task of ppfs data collection and documentation but the greater part will remain to be done; this and the generation of 'calibrated' data should be a first priority in any future work in this field. Further, although the generation of new data and the collection of ppfs data in general will continue to be a necessarily cooperative activity, it is felt to be necessary now to designate a ppfs centre in one or more COST countries. Such a step might lend itself best to *direct* or *indirect* action by the Community combined with *concerted* action so far as general participation is concerned. The centre would thus manage the data provided by the participants and disseminate them to participants (on specially favourable terms) and generally (on less favourable terms).

2. Contextualisation of ppfs Data

This subproject would endeavour to determine the degree of sensitivity of ppfs data to contextual factors likely to vary in normal circumstances. At first, those of general significance should be evaluated, followed by *all* the components, including 'inert' ones, and these should all be *quantified* where possible.

For example, it is known that, in general, values for the mechanical properties of foods are sensitive to the rate of deformation; that diffusivities of volatiles in foods are sensitive to the water content of the food. This being so, it is sufficient in the first place for those producing or using data to

be aware of the fact and to ensure that quantitative information on the contextual factor always accompanies the data.

The next stage would be to extend the list to (desirably) all contextual factors with at least a distinction between those known to affect and those believed *not* to affect the value of the ppfs under consideration. A third, or concurrent, stage would be to *quantify* the contextual effects wherever possible in order that due precautions in measurements may be taken and, more importantly, so that values for data may be *adjusted* to compensate for differences in context when using original data from elsewhere.

As this is likely to vary from property to property, a suitable subdivision of this work would be by property grouping as:

- (1) Liquid and solid properties.
- (2) Sorption and diffusional properties.
- (3) Electromagnetic including optical properties.
- (4) Thermal properties.
- (5) Other properties; common factors.

3. Applications of Data in Food Technology and Engineering

No apology should be needed for just increasing our knowledge and informedness about ppfs: they are needed by all who work with food. Nevertheless, the nature of the information needed varies from user to user and there are doubtless many whose work with food would be more effective if they were more aware of the contribution better use of ppfs data could make for them. A collaborative activity on these aspects would therefore aim to benefit directly the users and potential users of ppfs data. There might well be a case for approaching this aspect on a commodity group basis so as to identify from the outset the user's needs and criteria, but an alternative approach would be to look at the subject from the points of view of

- (1) product development,
- (2) process design,
- (3) equipment design,
- (4) process and plant operation and control, and
- (5) quality control,

although it would undoubtedly integrate better with other subprogrammes if the same property groupings as in (2) above were adopted. For example, there is increasing interest in the sorption properties of tropical produce on the part of both the producers and the users. This could as well be dealt with under the 'sorption' heading as under a commodity grouping.

4. Correlation of ppfs with Other Attributes of Food

There has occasionally been some pressure on COST 90/90bis to become involved with attributes of foods which are less explicitly 'physical' than are ppfs. Of these, sensory properties and quality attributes are, of course, extremely important to all concerned with food. Nevertheless, the decision has been wisely to avoid such complicating involvement within the limited resources and time scale of COST 90/90bis. What is proposed here is not that sensory properties and quality attributes as such be studied within this programme but rather that physical *correlates* of such properties be examined cooperatively, specifically *because* of their correlation with sensory and quality attributes. Because of the wide potential scope of such a study it is recommended that it be confined in the first instance to *correlates of texture*, as this is by far the clearest and most important interface between ppfs and other attributes of foods. Colour or, more generally, appearance is a special case in that the sensory attribute is directly due to the optical characteristics of the food. They are accordingly not *correlates* but the same attribute and are, of course, of great importance in both senses of that word.

4. ORGANISATION

The structure and *modus operandi* of the COST 90/90bis Projects, whilst not perfect, have served their needs well and something similar is proposed *faute de mieux*. The advent of the CGC structure within the Community and the fact that the proposed work might be part of the wider umbrella programme will need to be taken into account but, particularly in view of the experience accumulated within these Projects, it is most desirable that these two factors should not be allowed to change for the worse the *modus operandi* which has proved successful over the past 8 years. Although the work proposed here is new and important in itself, it does have its roots in the work of COST 90/90bis and many of the participants in those Projects will doubtless have important contributions to make to the new work and will benefit from continued use of a system of cooperation with which they are familiar.

There is at least one important lesson to be learned from the experience of COST 90/90bis, namely the absolute necessity that States formally committed to participation in the programme 'having willed the ends, must will the means'. This requires that participating States should, before they give their formal support, ascertain *clearly* and in detail what activities in

the fields of the Project exist or are planned in their countries; that these activities *are available* for commitment to the collaboration; and that the institutions and individuals involved will have at least the minimum financial and infrastructure support to enable them to make the appropriate contribution to the collaboration. This is so vital to the success of the Project that a period of time and adequate resources should be allocated to enable this detailed preparatory work to be completed well in advance of the actual commencement of the Project proper.

DISCUSSION

G. Smith: Sensory and organoleptic aspects are important. An ISO committee is working on Sensory Analysis and *G. Vos* is a member of it. Is it intended to liaise between ISO and any future work on this under COST? *G. Vos* was continuing to maintain contact with that ISO committee and it was intended to maximise liaison as and when the 'Umbrella' programme started. *R. Jowitt* counselled caution regarding sensory aspects by restricting, at least initially, COST work to identifying physical *correlates* of sensory attributes and the interface between them, rather than trying to work on both aspects simultaneously. *W. E. L. Spiess* concurred, saying that in his view *engineering* properties of foods had been emphasised in COST 90/90bis. Standardisation work could continue indefinitely, especially if sensory attributes were to be measured by engineers. Rather, he felt that newer areas should be tackled where understanding was incomplete by using input from different countries with their different ways of thinking and looking at problems. This he felt was always the greatest source of benefit to the participants. Regarding a European Data Centre, he felt that more than one would be found necessary, despite the undoubted attractions of a single centre. As a *European* action, several distributed centres would be necessary to reflect the diversity which would continue in the region. *F. Escher* recalled how 8 years earlier European food rheologists were aware mostly of American and Japanese work, but gradually, through COST 90/90bis, it became clear that a substantial body of competence existed within Europe and an important achievement of COST has been to make this known and familiar to many people. *D. A. E. Ehlermann* suggested that better results would be achieved in the future by workshops to which workers would bring their own instruments to make the same measurements on the same sample in the same place at the same time, and by an exchange of *technicians*—not scientists—between participating

institutions. They are most important people, they are the ones who actually *make* the measurements! True, all this requires funds but it would be better to omit a few meetings of scientists to pay for such arrangements. *Vos* referred to such an arrangement held in Lyons where many microbiologists were able to check microbiological methods at the same place without having to exchange samples at a distance. *Jowitt* referred to the time necessary to bring the working groups to a state of harmony and productivity. It was during this period that some of the most non-productive time was spent. Unfortunate but, in such diverse international groups, unavoidable. It was one of the important reasons for seeking to avoid a hiatus before the next phase and to retain the cohesion and teamwork now operative and which takes such a long time to achieve. He also proposed that early in any third phase of such work a meeting should be convened between European and North American workers in corresponding fields for the mutual benefit of participants and projects. Colleagues had benefited enormously from meeting personally fellow workers from other parts of Europe and stood to do so from similar transatlantic meetings.

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An Industrial View of COST 90bis

ERIK VON SYDOW

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I would like to start by quoting from my keynote address at the Dublin COST Conference of 1977:

'The average consumer spends the largest slice of her budget on food and related products. The food industry is, therefore, one of the largest industries in the western world. Raw materials, such as agricultural products and fish are, however, not necessarily available where the consumers are. They must be transported and, to allow transportation, they must very often be processed in industrial operations. This leads to trade, national or international.

International trade with foods basically is of two kinds: firstly, trade with raw materials, such as agricultural products and fish, and secondly, trade with industrially processed food products, such as cheese, deboned meat and frozen peas. The latter sector has increased through the years and different systems of food distribution, legislation, quality evaluation and consumer appeal have been confronted with each other as a result of this increased trade. Although many of the problems arising are of an economical and political nature, some important problem areas are to be found within food science and technology. Better understanding of such problems and solutions to the problems will promote trade of industrially processed food products and thus be beneficial to the food industry and allied industries and to the consumers.'¹

I shall not spend any time describing how the COST 90 and 90bis projects have developed, as this has already been done adequately by several contributors. However, I would like to draw your attention to what the *working party* laying the ground for these projects said strategically.

The working party agreed on certain criteria of importance for COST projects in the food technology area. These criteria were:

1. The project shall be an important contribution to research and development for the food industry and related industries.
2. The project shall draw specific advantage of the fact that several nations are involved.
3. The project shall stimulate industrial development and trade in Europe.
4. The project shall lead to improvements for the consumers.
5. The project shall give rapid and practical results for the industry.

As you will note, industrial aspects are referred to in several of these criteria and the question now, in 1986, is, of course: have the COST projects lived up to these criteria?

As usual, the answer can be given as 'yes' or 'no' depending on whom you ask and where you stand within the food industry.

To simplify things, we can divide industry in two blocks: the food producing industry and the food machinery industry. The latter group base their development work very much on physical data and, of course, also on requests from the food manufacturing industry. Both categories are dependent on good and solid research and development carried out partly by themselves but primarily at universities and R&D institutes. What industry does itself can only be a small part of what is necessary in total; public research and, to some extent, development is now and will in the future be of utmost importance for the food industry in general, including the food machinery industry.

It is quite obvious that the generation, compilation and distribution of physical data on foodstuffs is very important now and in the future for both the food machinery industry and the food processing industry wherever it takes place.

Have COST 90 and COST 90bis contributed to this? After discussions with a number of colleagues, the following partly negative and partly positive picture can be given. On the negative side, we observe that too little work has been spent on data processing systems and data outlet systems in comparison with work spent on measuring and collecting the physical data.

The COST 90 activities are not very well known among industry and I think that the local national groups can be criticised for this. More courses, more seminars, more lectures and articles based on COST work would have been desirable. Such activities should be stimulated. It has also been

proposed that more could have been done in conjunction with our US colleagues, where work in this field has been going on for many years.

On the positive side it can be noted that the COST 90 and COST 90bis projects have led to a much better cooperation among food science and technology institutions in Europe. Also that a lot of valuable data have been created which with suitable measures will become of great use to the food industry. Particularly important, as I see it, is also the part of the project which elsewhere has been called 'calibration of the participants'. For a food company with development and production of food products in many different countries, this is an extremely important aspect of the programme. The calibrated data produced are more reliable and usable across the borders.

Summing up, I would like to propose that the ongoing activities within COST 90 and COST 90bis be continued but that greater emphasis be put on data collection and data outlet systems on the one hand and on courses, seminars and lectures on the other. I would also like to propose that other physical properties be included but not necessarily too much in the area of correlating physical data with sensory data, at least not at this stage. I also think it would be important to create some kind of industrial reference group to help set up the priorities for future work.

However, all in all, I think industry can be quite satisfied with the COST 90bis and related activities.

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DISCUSSION

W. E. L. Spiess's experience was that, in Germany, industry was incapable of, or not interested in, relating to the Projects, despite his convening meetings and briefing representatives of industry. He would welcome a more formal or informal arrangement involving a contact group or groups from European industry, a group of advisers which would cost industry something, otherwise they would not appreciate it. *R. Jowitt*, referring to *E. von Sydow's* comment on relations between COST 90bis and work in

America, reminded the meeting that exactly 5 years ago an American colleague, Professor J. T. Clayton, had spoken favourably of the Project, as an observer from the USA, in the same position in the COST 90 Final Seminar as von Sydow that day. On the question of one centre versus several, he felt that fragmentation would be more costly in experts and more inefficient. It might have to be accepted but it should not be pursued as preferable in itself. However, single or multiple, it was gratifying to hear the support for such a centre or centres for ppfs in Europe. G. Vos said that CEC contacts with the European Food Industry Association in Brussels were at first weak but now were strengthening, as were their contacts with the IFT in the USA.

A Non-EC Country's View on COST

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The fact that Sweden has been involved in nearly 50 COST projects since the start of COST in 1971 has given us some experience and material for consideration. My views are based on a Swedish evaluation of completed COST projects within the areas of telecommunications, materials science and environment protection. What I say is also based on my own experience as an allocator of state funds to research work in food technology, and of course I have been in close communication with the Swedish participants in COST 90 and COST 90bis, and COST 91 and COST 91bis.

For a small country like Sweden it is necessary to have an international outlook and to cooperate with other countries in scientific research. There are different ways of doing this. The most common way is by bilateral cooperation. That requires very little extra administration. But a small country either had to be very smart or unique to be accepted as an equal partner by, for instance, Japan or the United States. Another way open for us is to cooperate within the Nordic countries. Short distances, kindred languages and other similarities make it easy to work together, and we can also obtain financial support from the Nordic Council. The disadvantage is that even together we are not a large group compared to the rest of the world.

I think it is important to keep these alternatives in mind when we are to judge the COST programmes. In Sweden we think COST is a good instrument for the conduct of international scientific and technological research. The main reasons are the principles on which COST is based.

They can be summarised as follows:

- COST constitutes a privileged framework for cooperation between the European Community and European non-member states in the field of research and development.
- In the framework of COST, joint research cooperation is carried out by 'concerted action', and financing is provided by the individual states.
- COST has no common research policy but functions *ad hoc*. This means that there is complete freedom of choice regarding projects and participation in them.

The intentions of the programme are without any doubt good. But what has been achieved? For a representative picture of that we have first of all to ask the scientists involved in the programmes and the industrialists utilising the results. We might also ask the allocators of funds if the results have been worth the money.

Scientists who have been involved in COST programmes, irrespective of area, are remarkably unanimous. The advantages they point to can be summarised as follows:

- Participation permits personal contacts with research workers in many countries.
- The possibility of visiting laboratories in other countries is of great value.
- The fact that many countries participate in each programme gives their research a wide framework.
- Personal contacts give quick access to new reports; there is no waiting for publications.
- The programmes have been a simple way of cooperating and a good introduction for young research workers to international research.

As for industrial utilisation, I believe Professor von Sydow's views of COST 90bis (Chapter 45) are valid for many other COST projects also.

As a representative of those who allocate funds, I must admit that COST projects are rather cheap in comparison with what we can get out of them. We Swedes pay only the Swedish contribution but receive the results achieved by others. Naturally, a prerequisite for obtaining the advantages is good programme leadership and active programme participation. As far as COST 90bis is concerned, we have been especially favoured in this respect.

So far I have been very positive about COST but obviously there are also disadvantages. The major complaint I have heard, and have been affected

by, is the planning time before a programme is definitely decided on. There are examples of programmes which have taken 5 years to plan. Both COST 90 and COST 91 took considerable time from when they were first suggested until they had passed through the process of all formalities. Of course, it is a good thing that each country has sufficient time to have a close look at the proposals and a chance to influence them. But after too long a planning time the expected financial and personal resources are no longer available—and maybe what we intended to do has already been done by the Americans or the Japanese!

As you can gather, in Sweden we have on the whole a very positive attitude towards COST and perhaps that is natural for a small non-EC country. The main reason is no doubt that we have the possibility of choosing whether we want to participate or not, and if we do participate we are allowed to cooperate as an equal partner. Against this background we look at the future with some apprehension.

We are well aware of the planning that is going on for the new Community Framework Programme of Scientific and Technological Research and Development, including an umbrella project for food technology. Even if most non-member countries have signed individual agreements about cooperation in this programme, there is great uncertainty about both how the cooperation within the Community will function and the future rôle of COST.

Summing up, I would like to say that our experience of the food technology programmes COST 90 and COST 90bis, and COST 91 and COST 91bis, have been very good and that a continuation would be valuable. The uncertainty about the status of non-member countries in relation to the food technology umbrella project planned by the European Economic Community in fact strengthens our conviction that continued cooperation is highly desirable. Sweden therefore supports Switzerland's proposal to form a Food Advisory Group within COST for the purpose of proposals and planning for extensive future European cooperation in the field of food technology.

DISCUSSION

F. Escher and *P. Linko* heartily concurred, for Switzerland and Finland respectively, with the proposals to set up a Food Advisory Group in COST. There was no doubt that political as well as technical activity was involved in achieving worthwhile action on scientific and technical matters in COST and the Community.

The Framework Programme of Community Activities in the Field of Research and Technological Development

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INTRODUCTION

It was exactly 5 years ago, on 11 September 1981, that Mr Contzen delivered the closing address at the COST 90 Final Symposium in the Catholic University of Leuven (Contzen, 1983). At the time he gave an overall view of the problems in the field of science and technology, and an outlook for the coming years. These 5 years have passed very quickly, and not only has the COST 90bis project been implemented very successfully but the whole science and technology policy of the Community has also been the subject of many discussions and decisions, sometimes at very high levels. It is my intention here to give some information on a few of the recent events.

Before doing so, I would like to thank—on behalf of Vice-President Narjes and Director-General Professor Fasella—the Department of Food Science in the Swiss Federal Institute of Technology for their work in organising this symposium. A special thank-you is also due to those who contributed to the success of the project: Dr Escher and Professor Jowitt, the Chairmen of Subcommittees, and, last but not least, the Secretariat, Mr Vos, and Mrs Sakaloglou.

Five years ago Mr Contzen spoke of the European crisis, the social and economic difficulties, and the way in which science and technology could help to overcome these difficulties. Today the situation has certainly improved, although a satisfactory solution for the problem of unemployment has not yet been found.

WHAT HAS BEEN DONE IN RESEARCH AND DEVELOPMENT?

- The first framework programme (1984–87), for Community research, development and demonstration activities, was adopted in 1983.
- A European Strategic Programme for Research and Development in Information Technologies—ESPRIT—was adopted in 1985.
- A multiannual research action programme in the field of biotechnology was adopted in 1985.
- A multiannual programme in the field of basic technological research and the applications of new technologies—BRITE—was adopted in 1985.
- A plan to stimulate European scientific and technical cooperation and interchange was adopted in 1985.

Furthermore, the preparatory phase for the programme of Telecommunication Technologies—RACE (Research in Advanced Communication Technologies in Europe)—was launched.

These are only examples of decisions taken in fields where the Communities, as such, had no programmes under way before. It is, of course, understood that activities have been going on in other fields, such as:

- radioprotection;
- thermonuclear fusion;
- management and storage of radioactive waste;
- non-nuclear energy;
- data processing;
- food technology (COST 91bis);
- environment;
- the programme of the Joint Research Centre (JRC).

But in a world characterised by the acceleration of the process of innovation, the global application of production techniques, the development of services and, lastly, the expansion of defence programmes and the importance attached to space in national technological development, Europe is beginning to organise itself.

The most important events have been:

- The Enlargement of the Community to 12 Members.

- The European Council meeting in Milan (June 1985), where the Commission's memorandum 'Towards a European Technology Community' was approved and adopted.
- The EUREKA ministerial conference in Hannover (November 1985).
- The European Council meeting in Luxembourg (December 1985), which inserted in the European Single Act provisions covering technological R&D activities.

This European Single Act provides a new political and legal basis for the development of the Community's scientific and technical strategy.

WHAT IS THE CONTRIBUTION OF THE COMMUNITY DISCUSSION TO TECHNOLOGICAL R&D IN EUROPE?

The Community provides a **framework for a synergy of efforts and abilities**; it thus promotes the **attainment of economies of scale and critical size** and provides the opportunity for diversification called for by rapid and expensive scientific and technical development.

The Community action creates **fertile soil for greater creativity and cooperation** on the part of the scientists and industrialists involved in strategic programmes and priority for significant projects.

The Community framework links efforts in the field of technology to the **large European market**. In 1992 it will lead to open public sector markets based on common standards and a common industrial property policy.

Lastly, the Community provides a coherent framework for the **optimisation of the efforts of the Member States**, the exploitation of their specific potential and avoidance of the **duplication of activities**, all of which benefit **both the Community as a whole and its individual regions**.

Community activity in the field of technological R&D will be conducted in a series of programmes at three levels, mainly:

- a unanimously approved multiannual Framework Programme** which will provide the basis for the balanced overall development of Community actions;
- specific programmes, adopted by a qualified majority**, which are concerned with particular objectives, designed to promote cooperation between all the partners and open to participation by non-member states;
- supplementary programmes** in which Member States will participate on a voluntary basis.

WHAT ARE THE PRIORITIES FOR COMMUNITY ACTION?

The Commission proposes the adoption of eight lines of action adapted to the new requirements of the 1990s. Community intervention in the field of R&D is particularly justified when:

- It serves to affirm and defend the European model within which the social dialogue, living and working conditions, and concern for the environment occupy a special place.
- It is directly linked with the creation of an enlarged and more competitive economic area.
- It contributes to the harmonious development of the Member States by drawing on the high-quality scientific and technological infrastructure that is the common property of all.
- It permits capitalisation on the acknowledged know-how already accumulated by the Community.

These objectives have served as a guide in the choice of the eight activities selected by the Commission for inclusion in the framework programme. These activities are set out below.

1. Quality of Life

Although this topic covers a vast area of research, the Commission intends to concentrate Community efforts on health and the environment.

2. Towards an Information Society

This research will concentrate on the following three areas:

- microelectronics and peripheral technologies;
- data-processing systems;
- applications technologies.

3. The 'Life Blood' of a Large Market

The introduction in the Community during the 1990s of integrated broadband services offering a wide range of services based on processing and transmission capacities and the ability to exchange data, text and images.

4. Application of the New Technologies in the Modernisation of Industrial Sectors

In particular, in the following areas:

- advanced design and manufacturing techniques;

- materials (ceramics, composite materials, etc.);
- techniques for exploiting raw materials.

5. Continuation and Updating of Activities in the Energy Sector

This applies to the following areas:

- Nuclear fission. The work will be concerned with the safety of reactors, the management of radioactive waste and the safeguarding of fissile materials.
- Thermonuclear fusion. The framework programme will include work on the scientific and technological feasibility of fusion reactors. For the period 1987–91, the principal objective will be to move forward to the NET concept (Next European Torus).
- Non-nuclear sources of energy and the rational use of energy.

6. Biotechnology

Particular attention will be given to the creation of a multitude of new relationships between agriculture and industry.

7. Exploitation of the Seabed and Use of Marine Resources

Up to now the national programmes have evolved separately. Community activities will seek to ensure the convergence of efforts aimed at developing the scientific and technological base necessary for the exploitation, management and protection of marine resources (both mineral and food resources).

8. A Europe for Research Workers

This will involve the gradual creation of a Europe for research workers, notably through the provision of support for further education, retraining and encouragement of mobility among research workers.

The scale of the challenge and the Community's ability to respond will necessitate an appreciable increase in the financial resources, both public and private, national and Community, made available for research and technology. For its part, the Commission puts the total financial commitments required for the implementation of the 1987–1991 Framework Programme in the region of 8000 Mio.ecus. Although this amount constitutes an appreciable increase in relation to the budget for the preceding Framework Programme, it represents less than 4% of total research expenditure in the Member States over the same period.

NEW ARRANGEMENTS FOR IMPLEMENTING COMMUNITY RESEARCH

Concerning the implementation of the well-known

- Concerted Action
- Shared-cost Action
- Joint Research Centre

the Commission is in favour of a significant increase in shared-cost actions of the ESPRIT type compared with the direct-action projects carried out at the Joint Research Centre.

In addition to those already established, new implementing arrangements will be prepared, for example the creation of **joint enterprises** or the initiation of **supplementary programmes** for which the European Single Act provides.

Community budgetary intervention will be supplemented by a number of facilities derived from new Commission initiatives in respect of financial instruments or techniques, particularly in the case of technological R&D programmes for industrial-scale application which are close to the market, such as the *Eureka Projects*.

CONCLUSION

The foregoing is a brief view of the content of the proposal for a Council Regulation relating to the Framework Programme of Community activities in the field of R&D from 1987 to 1991. This proposal has been preceded by another document of the Commission, namely *Guidelines for a New Community Framework Programme of Technological Research and Development (1987–1991)* (communication from the Commission to the Council and the European Parliament).

This has been discussed by the Council of Ministers for Research on 10 June 1986 in Luxembourg. As a result of these discussions, and taking into account the comments and wishes of the various Member States, the concrete proposal, of which I spoke earlier, was elaborated on by the Commission. For example, the overall budget figure was slightly amended from 10 000 to 7735 Mio.ecus; in addition, some new priority topics have been introduced, such as the 'exploitation of the seabed and use of marine resources' (Table 1).

TABLE 1
**FRAMEWORK PROGRAMME OF COMMUNITY ACTIVITIES IN THE FIELD OF RESEARCH AND
 TECHNOLOGICAL DEVELOPMENT (1987-1991)**
(Breakdown of the amount deemed necessary between the various activities
envisaged)

	<i>Million ecu</i>
1. <i>Quality of Life</i>	575
1.1. Health	150
1.2 Environment	425
2. <i>Towards an Information Society</i>	2 050
2.1. Information technologies	2 050
3. <i>The Life Blood of the Large Market</i>	1 120
3.1. Telecommunications	800
3.2. Integration of telecommunications technologies with information and broadcasting technologies into new services of common interest	300
3.3 Transport	20
4. <i>Application of the New Technologies to the Modernisation of Industrial Sectors</i>	1 110
4.1. Technologies for manufacturing industry	500
4.2. Science and technology of materials and raw materials	370
4.3. Technical standards, measurement methods and reference materials	240
5. <i>Continuation and Updating of Activities in the Energy Sector</i>	1 890
5.1. Fission	580
5.2. Fusion	1 100
5.3. Non-nuclear energies and rational use of energy	210
6. <i>Biotechnology: A New Technological Crossroads</i>	450
6.1. Biotechnology, management of agricultural resources, agro-industrial technologies, science and technology for development	450
7. <i>Exploitation of the Seabed and Use of Marine Resources</i>	80
7.1. Marine science and technology	80
8. <i>A Europe for Research Workers</i>	460
8.1. Implementation of a Europe for research workers	460
Total	7 735

The proposal for a Community Regulation concerning the *Framework Programme of Community Activities in the Field of Research and Technological Development (1987-1991)* was adopted on 24 July 1986 by the Commission and transferred to the Council. The British Presidency intends to have a decision made upon this before the end of 1986.

Clearly, different Member States have different problems, and decisions by the Community are influenced by these problems. Our Greek friends would probably like to see more research done on solar energy or earthquakes rather than high technology developments in nuclear fusion; Luxembourg is perhaps not as interested in the exploitation of the sea as others are. However, a decision will be taken and I hope that I have succeeded in showing you how much progress has been achieved for a European Community for Technology during the last few years.

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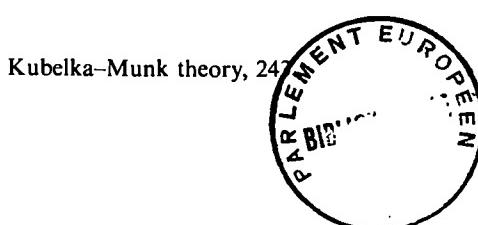
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This book, based on the proceedings of the COST 90bis Final Seminar, is a detailed account of the results of four years of European collaboration in the field of physical properties of foods. It is a sequel to the book *Physical Properties of Foods* which was based on the COST 90 Final Seminar of 1981, and deals with different subjects from those covered in the previous volume.

The first chapter is an overview of Project COST 90bis and the remaining chapters are divided into six parts, consisting of papers and adaptations of posters displayed at the Seminar. Transcripts of the discussions following the papers are also included. Part 1 comprises eleven chapters concerned with diffusion in foods and, as in the subsequent parts, includes a contribution from outside COST on a significant aspect of the subject. The eight chapters in Part 2 report on current and collaborative work on electrical properties of foods and their industrial significance. In the following eight chapters in Part 3 optical properties of foods are considered, in particular, collaborative 'calibration' experiments and practical and industrial significance of the colour of foods. Part 4, consisting of ten chapters, deals with the principles of and the COST collaborative work on the solid properties of foods including food powders, whilst the four chapters in Part 5 deal with the subject of data collection, handling and dissemination, both within and outside COST 90bis, and on food and non-food materials. The five closing chapters making up the final part, consider, in turn, some conclusions to be drawn from the Project's work, what should follow it and its relationship to wider issues.

ALSO OF INTEREST

Physical Properties of Foods

edited by R. Jowitt et al.

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Food Engineering and Process Applications

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Measurements in the Rheology of Foodstuffs

by J. H. Prentice

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